CHEMICAL STUDIES ON INLAND WATERS IN TASMANIA.

A THESIS SUBMITTED IN FULFILMENT OF THE REQUIREMENTS OF THE DEGREE OF DOCTOR OF PHILOSOPHY AT THE UNIVERSITY OF TASMANIA.

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BOTANY DEPARTMENT,

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DECLARATION

Exept as stated herein, this thesis contains no material which has been accepted for the award of any other degree or diploma in any University. To the best of my knowledge, this thesis contains no copy or paraphrase of material previously published by another person, except where reference is made in the text.

R. T. Buckney.

A C K N O W L E D G E M E N T S

I am grateful to my Supervisor, Dr. P. A. Tyler for his continued assistance and encouragement during this work, and to Professor W. D. Jackson and the staff and students of the Botany Department for their interest and assistance. Mrs. Rosemaree Wickham has been of considerable assistance with illustrations and generally around the laboratory.

Many people collected samples from inhospitable areas and in harsh weather conditions; I thank them for their cheerful cooperation. A few were of special assistance during the field study at Lake Dobson. Mick Macphail, Chris Harwood and Roger Croome are to be thanked for the work they did. Paddy Dalton on one occasion endured weather conditions which taxed his physiological tolerance.

Mr. Peter Murrell, Director of the National Parks and Wildlife Service was generous in providing a permit to operate on Lake Dobson. The Mt. Field National Park staff, particularly the Ranger, Mr. Rob Petrie, extended friendly cooperation.

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My scholarship was administered by Mr. David Arnold of the Department of Education; his assistance is gratefully acknowledged.

Christine Robinson, who typed the manuscript, deserves commendation for the patience needed to decipher my writing.

I am indebted to my friends, and more particularly to my family, for their constant interest and moral support.

CORRECTIONS

p.16, lines 9-10: replace the words "in some cases anomalous" by "many different".

p. 20: heading (C) should read (c).

p. 23: the figure caption should read "..IDEALISED TEMPERATE LAKE".

p. 24, line 4: replace the word "summer" by "dry period".

line 6: replace the word "winter" by "wet period".

p. 31, lines 18-19: sentence should read "... by the following regression equation found for Tasmanian waters: "

p. 32 et seq. : K18 should appear as K_{18}

line 7: after "condition" add "- saline waters may not (Williams, 1966)."

p. 34, line 1: After "Then:" add "(by Pythagoras' Theorem)"

p. 52, line 7: after "solubility" add "which have precipitated from solution".

Additional reference:

WILLIAMS, W. D. (1966): Conductivity and the concentration of total dissolved solids in Australian lakes - Aust. J. mar. Freshwat. Res. 17: 169-176.

S U M M A R Y

A simple scheme of major ion variability in inland waters is proposed, and is based on the assumptions

(a) that the relative proportions of the major ions (Stoichiometry) are controlled by the relative contributions of the atmosphere and the catchment to the dissolved matter in these waters and

(b) that total concentration is controlled by climate.

The published literature describing chemical changes in inland waters is explored for evidence in support of this scheme; it is concluded that sufficient examples exist for the acceptance of a normal or usual scheme of seasonal chemical change, though biological and other factors may obscure such changes.

A two-part notation describing the major ion chemistry of inland waters is derived and adopted to redescribe the chemistry of Tasmanian Waters. This notation is used to facilitate the investigation of some features of the variability of Tasmanian waters. Evidence is presented to show that climate is by far the most important determinant of variability of concentration, and that climate and geology are the most important factors affecting stoichiometric variability; morphometric factors are less important.

Outlines of models describing the chemical change in three waters are derived. These describe the main factures of the effects of

(a) flow regime

(b) flow rate and

(c) sediments on the chemistry of these waters.

C O N T E N T S

I N T R O D U C T I O N

1. RATIONALE

In chemical terms, inland waters are by far more diverse than other surface waters. Oceanic waters are substantially invariable as regards their total concentration and the relative proportions of the most abundant ions (Foyn, 1969); coastal marine and estuarine waters fluctuate in total concentration.

The total concentration of dissolved matter in inland waters ranges from less than 0.002 $g.l^{-1}$ (Williams et al, 1970) to more than 273 $g.l^{-1}$ (McLeod, 1963). The relative proportions of the most abundant ions also vary widely from water to water. Of the dissolved material, by far the largest proportion is made up of the major ions sodium, potassium, calcium, magnesium, chloride, sulphate and bicarbonate. Silicon is a further important constituent; other elements may be present in large quantities under certain conditions. The relative proportions of the major ions present are controlled by a number of factors (Gibbs, 1970; Gorham, 1961; Livingstone, 1963).

In addition to this chemical diversity of athalassic waters (sensu Bayly, 1967), there is a temporal variability evident within a given water. Variations in both total concentration and the relative proportions of dissolved constituents may far exceed those encountered in other surface waters. This chemical inconstancy of inland waters is one of their chief distinguishing characteristics. It is also one of their least studied aspects. Most studies on chemical variability have been restricted to a few substances of biological or economic significance, and have not usually been directed towards a clarification of the factors which control the chemical behaviour of these systems.

Two reasons may be suggested for this. First, it is difficult to manipulate the large amount of data (perhaps 10 or more variables per sample) obtained for a water sampled over a long period. Secondly, the chemistry

of natural aquatic systems may be "quite different from that predicted by laboratory experiments" (Morton and Lee, 1968). The first of these suggests the need for a simplification of the numerical presentation of a water analysis, while the second justifies an identification of the factors controlling chemical variability and their quantitative importance. These tasks are attempted in this thesis.

2. APPROACH

Inland water chemistry has been documented in a number of surveys; Gorham (1961) and Livingstone (1963) have nominated as the main controlling factors: climate, geology, catchment and water body morphometry, biology, age of the system and the supply of soluble matter from the atmosphere. The proposal of Gibbs (1970) - that the most important of these factors are climate, geology and the supply of salts from the atmosphere - allows a relatively simple scheme of seasonal variation to be postulated.

Gibbs (1970) claimed that an arid climate produced waters of high total concentration by evaporation. Thus, it would be expected that a given water would display an increase of total concentration during the dry part of the year, and a decrease during the wet period. If the relative proportions of the major ions are determined by the relative contributions of salts from the catchment and the atmosphere, as stated by Gibbs, then it would be expected that geologically-derived ions would become more important components of an inland water solution during the wettest months - in particular, when there is a net runoff from the catchment; atmospherically-derived ions enter a water at all times, either as dry fallout, or in the rain (Cassidy, 1968).

This simple scheme of variation is probably inadequate to account for all changes in real systems, but perhaps is a useful point from which to observe and account for anomalies. The main departures from this scheme might be expected to be related to biological activities.

The broard concept of Gibbs (1970) has been applied to a description of the chemistry of Tasmanian waters (Buckney and Tyler, 1973a), though in a qualitative way only. The quantitative representation of geological influences as used by Gibbs is not entirely satisfactory (Tyler, 1972), though it provides one basis on which to construct a simplified numerical representation of a water analysis. The concept relates total concentration to climate and the relative proportions of the major ions to the relative contributions of the lithosphere and atmosphere in supplying dissolved ions. Since in the absence of geological contributions and also in highly saline waters the relative proportions of major ions are usually like those in seawater, it should be feasible to describe inland water chemistry in terms of:

(a) total concentration and

(b) the degree to which the relative proportions of major ions differ from those of seawater. This approach has been adopted in this thesis.

3. PRESENTATION

(A) Organisation

The results of some studies undertaken by me have been published; reprints or copies of these are included in Appendix 2. No further discussion of these is presented here.

The unpublished part of this thesis explores aspects of the variability of major ion chemistry in athalassic waters, and is in four main parts referred to as chapters - each written in a form to facilitate later publication. Chapter 1 is a literature survey in which data are discussed under the headings: total concentration and the relative proportions of the major ions. This organisation is formalised in Chapter 11 where a binary numerical representation of water analyses is developed and its effectiveness in describing the features of Tasmanian waters is explored. Chapter 111 is a quantitative assessment of the variability of the two components of the binary notation and of the extent to which certain environmental factors contribute to such variability in a few waters. Chapter 1V is in three parts which deal with the chemistry of Granton

Lagoon, the Derwent River and Lake Dobson; in these, some points made in earlier chapters are investigated.

A concluding section is followed by an appendix which is a brief summary of a paper being prepared by myself and Dr. Tyler; it is referred to in the text as Buckney and Tyler, unpublished.

(B) Terms and Abbreviations used.

Throughout this work I have used the term stoichiometry to mean "the relative proportions of the dissolved major ions: sodium, potassium, calcium, magnesium, chloride, sulphate and bicarbonate".

The term equivalent concentration is used to denote the concentration of an ion in chemical equivalents per litre. For most purposes it has been found convenient to express concentrations in μ equ.l^{-1} (this is the same as μN).

Abbreviations

J.T.U. : Jackson turbidity units (or Formazin turbidity units).

K_{18} : the conductivity of a water at 18°C, (usually expressed in μS cm^{-1}; i.e. μ mho cm^{-1}).

n : number of samples

p.p.m. : parts per million, mg kg^{-1} (mg l^{-1}).

r : regression coefficient

S : Salinity, defined here as the sum of the concentration of major ions in mg l^{-1}.

Sx : (note subscript) Standard deviation of x

TDS : total dissolved solids, the weight of residue left after evaportion of a known quantity of water (usually in p.p.m.).

Vx : Variance of x.

X : relative proportion of the ion of element X.

(X) : Equivalent concentration of the ion of element X.

‰ : Parts per thousand, gm kg^{-1} (gm l^{-1})

Σ^+ : Total cation equivalent concentration (in μ equ l^{-1} unless stated otherwise)

Σ^- : Total anion equivalent concentration.

The term alkalinity has occasionally been used as a synonym for bicarbonate concentration. Where ions other than bicarbonate are thought to contribute to total alkalinity (sensu Golterman, 1969), the particular ions are nominated.

4. MATERIALS AND METHODS

(A) Sampling

Surface samples of water were taken by submerging acid-washed poly- - ethylene bottles to a depth of about 10 cm. Sub-surface samples in Lake Dobson were obtained with a 5-litre capacity closing sampler of the van Dorn type. Lake temperature and dissolved oxygen values were determined electrometrically with a Mackereth (1964) type probe.

Mud samples were taken with a Petersen grab. Interstitial water was obtained by vacuum-assisted filtration of the mud, using Whatman filter paper (No. 542).

Untreated samples were stored at 5-10°C in the dark upon return to the laboratory.

(B) Analytical

Alkalinity was determined in conjunction with pH using a Radiometer pH 26 meter and automated titration equipment. Titrations were with 0.01N HCl to an automatic end point of 8.3 (for carbonate) or 4.5 (for 'bicarbonate'); for Lake Dobson an end point of 4.9 was employed (after Golterman, 1969). Conductivity was determined electrometrically on samples maintained at 18°C in a water bath. Turbidity was measured with a Hach 2100 Turbidimeter. All other determinations were made on waters filtered through membrane filters of 0.5 μm

pore size, and suitably diluted with glass-distilled water.

Colour was estimated in Hazen (or platinum) units by comparison with glass disc standards in a BDH Nessleriser with standard white-light illumination. Silicon concentration was determined as "molybdate-reactive silica" using the molybdate yellow method (American Public Health Association, 1971).

The ion-exchange-conductometric method was used for sulphate measurements (Mackereth, 1963). Chloride concentrations were determined by automated conductometric titration with silver nitrate (Golterman, 1969).

All metallic elements were determined by atomic absorption spectroscopy, using a Varian AA5 instrument.

Statistical operations were performed on a Hewlett-Packard Model 10 calculator.

The above methods were employed after 1971; some earlier analyses were performed in slightly different ways, as described by Buckney and Tyler (1973a, 1973b). No substantial differences in analytical results were noted, although the later analyses showed a slightly smaller anion excess than the earlier ones.

(C) Observations on Analytical Reliability and Results

The majority of the analyses showed a balance of anions and cations which was acceptable (American Public Health Association, 1971). The greatest deviations occured among saline waters and some for which alkalinity was very high. Buckney and Tyler (1973a) attributed an excess anions phenomenon to an interference by solid matter (after Golterman, 1969). Subsequent (non-rigorous) investigations have made it obvious that this assertion was wrong. It is possible that organic components of the water solution interfere, or that free CO_2 obscures the end point. Ion pairing is not considered likely to be significant in dilute waters (Morton and Lee, 1968). Some features of the phenomenon are summarised briefly below:

1. The phenomenon seems to be restricted to waters for which the cation concentrations are in the order : $Na \rangle Ca \rangle Mg \rangle K$, and

then only for waters in which Ca is less than about 30% of the cation equivalent concentration.

2. During the titration, the pH is maintained at about 6.3 for a long period, this being (presumably) the time when most of the "excess" acid is added, and implies the existence of a secondary equivalence point at a pH above 6.3.

No formal attempt has been made to correct the problem. The procedure adopted has been simply to reduce the alkalinity figure to that which would ensure that the sum of the equivalent concentrations of the cations equals the sum of the equivalent concentrations of anions.

Among saline waters, a similar phenomenon has been noted. This relates, however, to the chloride ion. It is thought that organic components interfere with the $AgNO_3$ titration. This chloride excess has been noted to occur only sporadically even within a single water. Different waters of comparable salinity sampled on the same day do not all display the analytical excess, so it is unlikely to be the result of a simple analytical error.

Calcium has been determined in an air-acetylene flame. Amos (1970?) and Fishman and Downs (1966) have reported that the elements P, S, N, Si and Al form refractory compounds in an air-acetylene flame, and have recommended the use of a hotter flame or the addition of a releasing agent (usually $LaCl_3$) to minimise this effect. The effects of a series of concentrations of P, S, N, and Si were assessed for a solution containing 5 p.p.m. of Ca; Si caused a measurable decrease of absorbance at 25 p.p.m. and S (as sulphate) at 15 p.p.m. Nitrogen and phosphorous had no measurable effect at concentrations up to 10 p.p.m. It was assumed that such interfering concentrations of these elements would not be encountered in the dilute solutions to be analysed, and the air-acetylene flame was used for convenience.

Mackereth's (1963) method for sulphate determination has not given results which are entirely reproducible (up to 20% spread at high concentrations). The

procedure adopted was to callibrate each new exchange column as it was prepared. The method was found to be acceptable at low total concentrations of ions.

Flow readings were taken by the Hydro-Electric Commission for the catchments in which these are quoted. Responsibility for these measurements was transferred to other bodies at some stage during this study, and flow data for the later part of the study are not yet available.

CHAPTER 1

SOME ASPECTS OF THE VARIABILITY OF MAJOR ION CHEMISTRY IN INLAND WATERS

CONTENTS

ABSTRACT

The literature dealing with variability of chemical conditions in inland waters is reviewed.

Diurnal, seasonal and long term variations in major ion chemistry are examined and discussed. An interpretation of the published information is presented in terms of total concentration and stoichiometry of the water. The main factors proferred as controls on variability are identified. A pulse phenomenon relating to the effects of the first runoff after a dry period is recognised.

A simplified and generalised model of the chemical behaviour of an idealised lake is presented, together with a discussion of its most obvious limitations.

1. GENERAL CONSIDERATIONS

The treatment by Gibbs (1970) of inland water chemistry would suggest that climatic variations would account for most of the variation of chemical conditions in a body of water. Such climatic variation would be effective through its interaction with the geology and the supply of salts from the atmosphere. Other factors may be important; Gorham (1961) listed atmospheric supply of ions, climate, geology, topography, biology and time as affecting inland water chemistry; of these, biological factors may cause variations which are not directly related to the three major influences described by Gibbs.

2. THE LITERATURE

The small quantity of useful literature describing variations in major ion chemistry in inland waters has not been presented in a consistent manner. Problem substances have often been treated in detail (e.g. Butcher et al., 1939; Tyler and Buckney, 1973) without comparable reference to major ions. Usually, the data have been presented in a derived or graphical form, sometimes without comment. Hence, much of what follows is the interpretation of this author.

Three basic types of variation can be recognised; these are:

(A) Diurnal (B) Seasonal (C) Secular or long-term changes.

These constitute the headings under which the topic is treated.

(A) Diurnal Variations

These have usually been attributed to the effects that the physiological responses of organisms to daily changes in light intensity and temperature have on water chemistry. They include

(i) a daytime rise of pH and night-time fall (Ganapati, 1969; Hussainy, 1967; Kelso and Maccrimmon, 1969) related to the

effects of photosynthesis and respiration on the carbonate-carbon dioxide equilibrium in water (Butcher et al., 1939; Dunn, 1967; Schute and Elsworth, 1954).

(ii) a related day-time fall of alkalinity and of conductivity (Carpelan, 1967)

and (iii) a night-time rise in phosphate concentration in response to bacterial activity (Canning and Walff, 1969).

Such changes could be expected wherever photosynthesis is intense in a water body: during algal blooms and where vegetation is flooded to a small depth. Intense respiratory production of carbon dioxide by organisms utilizing organic substances might obscure such changes (George, 1961).

Other ionic constituents of inland waters do not appear to have been investigated for evidence of diurnal variations, though in marl lakes the above mentioned changes could induce variations in calcium concentration as $CaCO_3$ is precipitated during the day and perhaps redissolved during the night as carbon dioxide becomes more plentiful.

(B) Seasonal Variations

Seasonal changes have been more frequently documented than diurnal changes. The topic can be treated conveniently under the headings (i) total concentration and (ii) relative proportions of the major ions (stoichiometry). Changes attributable to the cycle of stratification and holomixis are not considered below; they have been intensively treated by Hutchinson (1957).

Some factors controlling seasonal variation have received universal recognition, though much of the treatment of these has been purely qualitative. Details of changes or the existence of anomalies have often not been highlighted.

(i) Total Concentration

(a) Climate. Some authors have asserted the importance of climatic variation in controlling the variation of concentration in inland waters (Bayly and Williams, 1966; Hammer, 1965, 1971; McColl, 1972; Yaalon, 1964).

Many have observed high concentrations during the dry period (Ahl, 1966; Buckney and Tyler, 1973b; Cheng and Tyler, 1973a; Forbes and Allanson, 1970; Timms and Brand, 1973; Weatherley, 1958) or low concentrations during the wet part of the year (Anderson, 1970; Croome and Tyler, 1972; Morgan and Kalk, 1970; Moss and Moss, 1969; Viner, 1969). Some have qualitatively recognised an "inverse relation" between water depth and total concentration in endorheic systems (Howard-Williams, 1972; McLachlan et al., 1972; Pollard, 1971; White and Hartland- Rowe, 1969) and in rivers (Egborge, 1971; Imevbore, 1970). Langbein (1961) analysed the relation between the salinity and hydrology and other factors for closed lakes.

Hynes (1972) quoted the equation of Leopold et al. (1964), relating total concentration, T, to some power, f, of discharge, D, in rivers:

$T = KD^f$, where K is constant and f less than 1; he inferred that total concentration is high when discharge is low. No comparable equation has been applied to lakes.

Overall, the accepted notion is that total concentration rises during the dry season, and falls during the wet months (as shown in Figure 1.1, p.23). Williams (1962, 1967) recognised this as the usual case for Australia, but stated that a number of variations from the normal pattern may occur.

Factors which can act to obscure seasonal changes include:

(i) the freezing of lakes in winter, causing large rises in total concentration (Alexander and Barsdate, 1971; Boyd, 1959; Hammer, 1971; Howard and Prescott, 1971; Northcote and Halsey, 1969); this effect may be quantitative (Ahl, 1966).

(ii) the delaying of inflows by groundwater retention (Bayly and Williams, 1966; Pollard, 1971) or by a late snow melt (Anderson, 1970).

Timms (1970a, 1970b, 1973) emphasised that floods or showers obscured seasonal changes in TDS. The effects of the first inflows after a prolonged dry period are often considerable, and are sufficiently consistent to be treated separately.

After a dry period, the first runoffs often have an unusually high total concentration of dissolved salts which in the short term can indicate an anomalous positive correlation between volume of water and total concentration (Buckney and Tyler, 1973b). Thus, rises in concentration have been observed for the first stages of

(i) rises in lake level (Buckney and Tyler, 1973b; McLachlan, 1970; Morgan and Kalk, 1970; Moss and Moss, 1969),

(ii) floods in rivers (Coche, 1969; Egborge, 1971; Schmidt, 1972), and

(iii) the leaching of unsaturated soils by rain (Green, 1970). Later inflows result in dilution of the solutions, so that the receiving waters are subjected to a pulse of dissolved materials.

For a flood in the Danube, Dvihally and Vagas (1970) stressed the importance of flow regime (i.e. whether flow was increasing or decreasing) in determining the relation between discharge and water chemistry; they found that an ellipsoidal loop best described the relation between chloride concentration and discharge. Similar curves could be expected for other substances.

Pulse effects might be sufficiently intense to invalidate the equation of Leopold et al. (1964) quoted above, and probably explain a number of 'anomalous' changes in total concentration. Salts contributing to the pulse would be those which accumulated by weathering or evaporation in the catchment as water receded during the dry period (Morgan and Kalk, 1970) and those derived as dry fallout from the atmosphere (Cassidy, 1968; Ruttner-Kolisko, 1966).

(b) Other Influences. Some factors other than climate have been proposed as controlling the variability of concentration in inland waters. Largely, these have been morphometric features such as:

(i) lake volume (Bayly, 1970), surface area to volume ratio (Blinn, 1971) or mean depth (Hammer, 1971),

(ii) catchment area / lake surface area (renewal ratio) (Timms, 1970a), or an equivalent term (Cheng and Tyler, 1973a; Croome and Tyler, 1972

These influences have not been assessed quantitatively.

Bayly and Williams (1966) noted the greatest absolute and relative changes of TDS in lakes for which TDS never fell below 10‰. They disclaimed the inference that there is a strict correlation between (mean) salinity and its variation.

(ii) Stoichiometry

Since at different times and over wide areas, saline waters have displayed a near - seawater stoichiometry (Bayly and Williams, 1973; Cole, 1968; Langbein, 1961; Williams, 1964, 1967; Williams et al, 1970) it is reasonable to treat them separately from fresh waters, although in some cases anomalous compositions have been observed (Bayly and Williams, 1973; Hutchinson, 1957; Kilham, 1971).

(a) Saline Waters

Langbein (1961) described the expected precipitation of the least soluble salts (alkaline earth carbonates) in closed lakes, but recognised that the remaining constituents formed solutions of very stable composition despite substantial changes in lake volume. This stoichiometric stability has been recognised by Bayly and Williams (1967), Blinn (1971), Cole (1968) and Walker (1973). These observations record a behaviour which is not as expected of a simple inorganic mixture (see Hutchinson, 1957), and allow the suggestion that solubility limits for inorganic ions in such situations are modified - perhaps by organic components of the solutions. This would be a significant deviation from the behaviour predicted from the shceme of Gibbs (1970).

Despite their stoichiometric stability relative to fresh waters, saline waters have commonly exhibited certain changes. Thus, during increases of salinity, there have been observed:

(i) rises in potassium proportion (McLachlan et al. 1972; Morgan and Kalk, 1970; Walker, 1973),

(ii) falls in calcium proportion by precipitation of $CaCO_3$ (Blinn, 1971; Howard-Williams, 1972; McLachlan et al., 1972; Morgan and Kalk, 1970; Moss and Moss, 1969),

(iii) rises in pH and alkalinity (McLachlan et al., 1972; Morgan and Kalk, 1970; Weir, 1968) resulting in increased dominance by carbonate (Anderson, 1958; Blinn, 1971).

Astatic waters may be more variable than permanent ones (Blinn, 1971) and probably less consistent in their behaviour. Thus pH has been recorded to fall during a dry period (Blinn, 1971) in some temporary lakes, and to rise in others (White, and Hartland-Rowe, 1969). Waters with anomalous stoichiometry may behave abnormally (Blinn, 1971).

Most permanent saline waters can be expected to show falls in calcium (and perhaps magnesium) proportion during the dry months, with rises in pH and the proportions of potassium and alkalinity. The alkalinity rise might represent the evaporative concentration of contributing ions at a rate greater than primary producers can utilize them.

(b) Fresh Waters

There are few reports which describe the variability of more than one or two components of fresh water solutions. The following survey initially deals with the relative proportions of the major ions (i.e. stoichiometry) and later touches on the behaviour of ions in waters for which inadequate data on total concentration are available.

A number of authors hae illustrated proportionate rises in one or more of the ions: calcium, magnesium, sulphate and bicarbonate during the wet months (Ahl, 1966; Cheng and Tyler, 1973a; Egborge, 1971; Howard and Prescott, 1973; McColl, 1972; Timms, 1970a; Viner, 1969; Yaalon, 1964). Silicon and nitrate have been reported to behave similarly (Egborge, 1971); these almost certainly are controlled by biological factors during the summer (e.g. Cheng and Tyler,

1973b) as are calcium and bicarbonate levels in marl lakes (Otsuki and Wetzel, 1974).

It may be argued that the effect of the dry season is to cause a reduction in the proportion of geologically derived ions. During the dry period, biological effects are most important, and catchments are likely to absorb most of the rain falling on them, so that most water entering the water body falls directly on the water surface.

Some exceptions to this behaviour might be related to the effects of organic matter in the water (Buckney and Tyler, 1973b; Munawar, 1970) or to abnormal rainfall patterns (Croome and Tyler, 1972). Where groundwater is a major source of calcium, the concentration of that element may be greatly reduced temporarily by rainwater falling directly on the water surface (Grimshaw and Hudson, 1970; Otsuki and Wetzel, 1974).

Maxima of pH are usually observed during the summer months (Buckney and Tyler, 1973b; Castenholz, 1960; Hammer, 1971; Hussainy, 1967; Imevbore, 1970; Kelso and Maccrimmon 1969; McColl, 1972; Timms and Midgley, 1969; Venkateswarlu, 1969; Weatherley, 1958), probably as a result of increased photosynthetic activity; the appearance of pH maxima at other times of the year may be associated with inflows of nutrients (Bradley and Beard, 1969; Egborge, 1971) or their release from sediments under ice (Ahl, 1966; Anderson, 1970; Boyd, 1959).

Photosynthetic utilisation of carbon dioxide may cause a proportionate fall in alkalinity during the summer (Alexander and Barsdate, 1971; Woldike, 1973), though proportionate rises may occur, at least initially (Buckney and Tyler, 1973b; Croome and Tyler, 1972; Hussainy, 1967; Imevbore, 1970; Munawar, 1970; Timms, 1970a; Weatherley, 1958; Yaalon, 1964) as a result of respiratory release of carbon dioxide or through an effect of the sulphur oxidation-reduction cycle (Mann, 1958).

Colour intensity has been shown to increase during the summer (Bradley and Beard, 1969; Gjessing, 1966), perhaps as a secondary effect of the usual pH rise (Bayly, 1964; Hutchinson, 1957).

Sediments have been implicated as a factor in stabilizing the stoichiometry of a shallow lake relative to nearby lakes (Buckney and Tyler, 1974). Lerman and Brunskill (1971) estimated that up to 30% of the major cations in two shallow lakes come from the sediments.

In most regards, saline and fresh waters appear to behave similarly, with the likely exception of alkalinity. Geologically-derived ions show a proportionate fall during the summer months while pH rises. This behaviour is summarized at the end of this chapter in Figure 1.1

Pulse processes have shown some consistent stoichiometric features which include (i) rapid falls in pH and alkalinity proportion (Buckney and Tyler, 1973b; Egborge, 1971; Imevbore, 1967, 1970; Morgan and Kalk, 1970; McLachlan, 1970; Michael, 1969; Timms, 1973; Timms and Midgely, 1969), though exceptions have been noted among saline waters (Howard-Williams, 1972; Weir, 1968)

(ii) proportionate rises in sodium and/or potassium (Buckney and Tyler, 1973b; Howard-Williams, 1972; McLachlan, 1970), though an exception is obvious (Imevbore, 1970);

and :- (iii) intensification of colour (Buckney and Tyler, 1973b)

(iv) marked increases in the concentrations of:

silica (Imevbore, 1967),

phosphate (Howard-Williams, 1972; McLachlan, 1970; McLachlan et al, 1972; Moss and Moss, 1969; Serruya and Pollinger, 1971),

and nitrate (Egborge, 1971; Munawar, 1970; Park et al., 1970).

Gorham (1961) described the selective leaching of the more soluble salts from

catchments after a dry period and nominated chloride as the most mobile ion.

A seasonal variation in the diurnal change of pH has been recognised; the diurnal range of pH is greatest during the summer, when the daily maximum is highest and the daily minimum lowest (Butcher et al., 1939; Kelso and Maccrimmon, 1969; Michael, 1969).

(C) LONG-TERM (SECULAR) CHANGES

Secular trends in total concentration of inland waters have been related to concurrent changes in climate for a few areas (Bayly and Williams, 1966; Hammer, 1965, 1971). Shorter-term trends have also been recognised (Bayly, 1970; Cheng and Tyler, 1973a; Pollard, 1971; Walker, 1973). Langbein (1961) and Hutchinson (1957) summarised some expected long-term processes in closed lakes.

Stoichiometric trends have not been as readily recognised. Bayly and Williams (1973) queried Hutchinson's assertion (1957) that the long-term trend in closed lakes is for the establishment of magnesium dominance. Hammer (1971) and Zyblut (1970) observed a trend for magnesium, chloride and sulphate proportions to rise during concentrating periods, the latter also noting a rise of pH for a lake that had increased in trophic status. Proportionate rises in magnesium and bicarbonate occured in a diluting phase in Tasmania (Cheng and Tyler, 1973a).

Newly-formed lakes may display persistent trends in chemical character, such as : (i) the enhancement of colour (Gjessing, 1966), and

(ii) the enrichment of solutes (Cooper et al., 1971). Sreenivasan (1970) claimed that pH and bicarbonate concentration would be expected to increase in the long term; Wilroy and Ingols (1964) recorded an apparent stabilisation of alkalinity in less than one year.

Rodhe (1949) postulated that freshwaters tend to attain the world average freshwater composition (see Livingstone, 1963) under the influence of chemically-

exchanging lake sediments. Gorham (1955, 1961) has critically discussed this proposal and emphasised the importance of ambient influences in determining water chemistry.

3. DISCUSSION

(A) General

If the scheme of Gibbs (1970) was relevant to a consideration of the variation of major ion chemistry in inland waters, total concentration would be expected to rise during the dry period and be accompanied by a stoichiometric displacement towards seawater. The literature provides a number of examples of that behaviour, but exceptions are quite common.

The increase of concentration during a winter freeze differs from evaporative concentration only in the means by which liquid water is removed from the lake. Stoichiometric differences between the two concentration processes would largely reflect the differences in solubility of salts at the different temperatures involved.

The diurnal and seasonal changes in pH are governed largely by biotic influences, and this is a major feature which the Gibbs assessment does not incorporate. Biotic controls also apply to alkalinity: intense respiratory consumption of organic compounds may offset the utilisation of carbon dioxide by primary producers. Apart from the obvious influences it exerts on nutrient concnetrations, the biota may also influence the stoichiometry of salting solutions, and diurnal changes in calcium concentration. Hence, a consideration of chemical variability of inland waters ought to deal separately with pH (at least).

The pulse phenomena are further departures from the Gibbs scheme. These probably occur as a result of the fact that after active water transport ceases in a catchment, weathering of rocks and soils continues (at least until all the retained water evaporates); the salts released under these conditions are then all removed with the next runoff at rates determined by their solubilities.

The intensity of a pulse effect is probably proportional to the time between saturating rains. A corollary of this consideration is that during a prolonged wet period the rate of weathering of rock could be sufficiently small to ensure that atmospherically-supplied ions come to dominate the later runoff.

The literature as a whole strikingly displays the need for study of the relation between flow rates and water chemistry. Two sorts of relations can be predicted:

(a) the pulses in which the supply of weathered materials is sufficiently great to ensure that the solubilities of the leachable salts control the chemical nature of the runoff and

(b) cases where weathering is slow and water availability is high so that flow rate determines the chemical character of the water. Pulses would be expected to predominate in more arid areas, and to be relatively rare events in humid areas.

At this stage, a description of the chemical behaviour of an inland water can only be superficial and based on a highly idealised and simplified model. Such a model is presented below by way of a summary of the above review.

(B) An Outline of a Model Describing the Seasonal Behaviour of the Major Ions in Inland Waters

In Figure 1.1 are assembled some simple, idealised curves for a theoretical lake with the following characteristics:

(i) the lake is small and shallow;

(ii) the catchment area is large, and of weatherable rock;

(iii) the sediments are chemically inactive;

(iv) the lake is productive, but does not contain large quantities of organic matter

(v) the lake does not dry out completely, and overflows during the wet period.

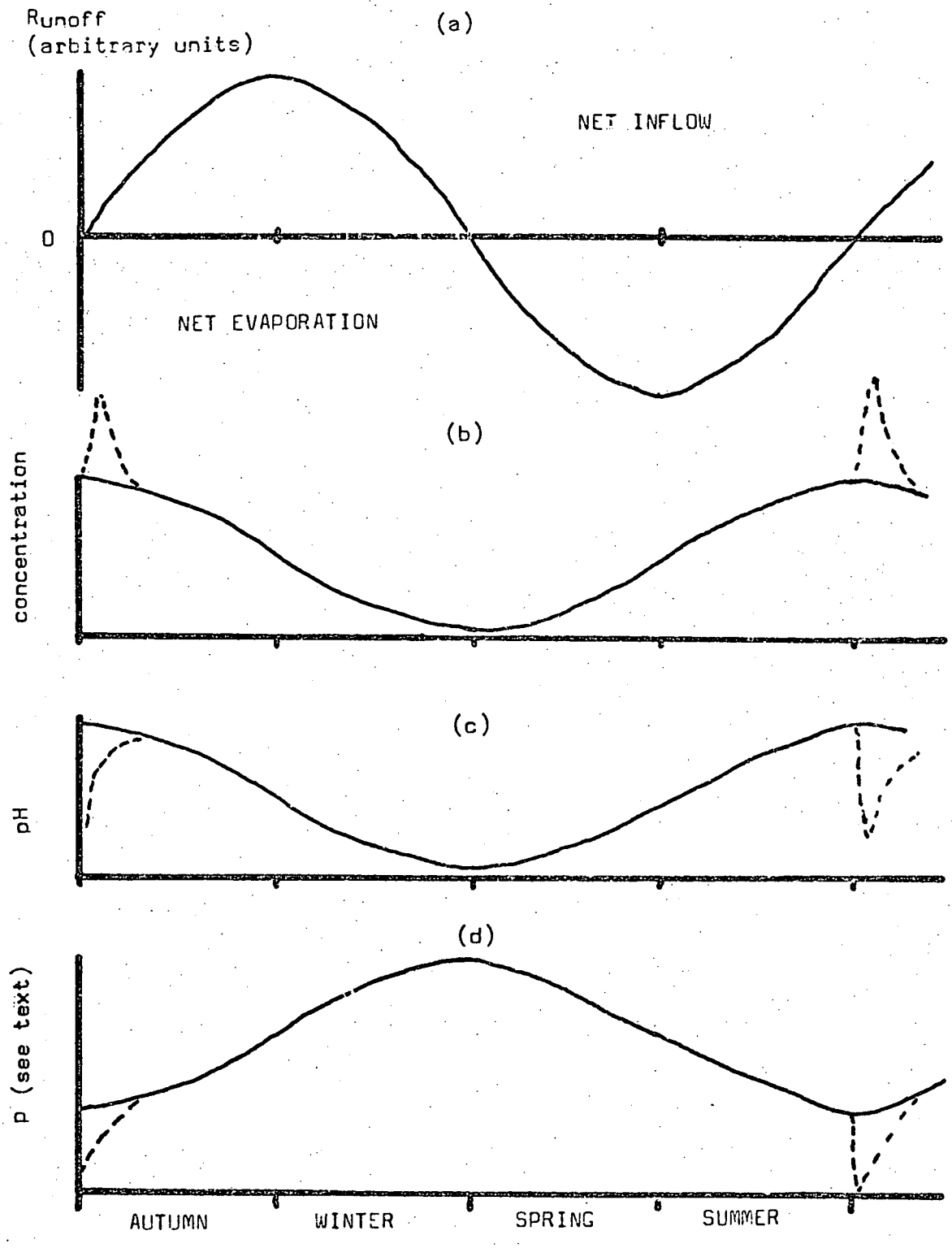


FIGURE 1.1 : THE EXPECTED OR NORMAL PATTERN OF SEASONAL CHEMICAL CHANGE IN AN IDEALISED LAKE (see text).
Dotted lines show pulse behaviour.

If the simplistic seasonal variation of runoff as shown in Figure 1.1(a) applies to this lake, then total concentration would decrease while there was a net inflow of water and increase during the net evaporative loss (Fig. 1.1 b). Utilisation of CO_2 during the summer would result in an increase of pH, while the increased relative importance of respiration and mineral equilibria during the winter would be expected to cause a decrease of pH (Fig. 1.1 c). During the concentrating period - when the atmosphere is the only significant source of dissolved material - the water would approach a stoichiometry like that of seawater. A pulse would be expected with the first inflow of the wet season; its possible nature is represented by the dotted lines in Figure 1. During the pulse, pH would be expected to fall and total concentration to rise, while the water would tend to attain a stoichiometry similar to seawater.

If it is assumed that there is some parameter, P, which represents the stoichiometry of the water such that when the stoichiometry is like that of seawater, P is small and when unlike seawater, P is large - as shown in Figure 1.1(d) - then the curves in the above figure allow the suggestion that P might be correlated with the negative or inverse of total concentration and of pH for most of the year.

During the pulse period, relations between these parameters can be anticipated to be more complex. The ellipsoidal loop described by Dvihally and Vagas (1970) as the best available description of concentration changes during a flood might be approximated by two intersecting straight lines; one of these lines would apply to the period of increasing flow, and the other to the period of decreasing flow. A possibility is that during such periods the water chemistry is at least partially defined by the rate of change of flow.

The model above is highly simplified, but it facilitates the presentation of some conclusions. The main factors which will act to invalidate the model have been discussed previously. The simplistic pattern of runoff changes

allows the admission of only one pulse effect during the year; real cases might include several such phenomena of varying intensity through the year. Biological factors may cause changes in parameters other than those nominated.

It is evident that an investigation of chemical variability would be simplified if some parameter (like P, above) representative of stoichiometry could be used. One such parameter is derived in the following chapter, and some of its properties explored.

4. CONCLUSIONS

1. Total concentration can be expected to rise during a dry period, and to fall while runoff enters a water body.

2. Salinity may rise in winter when water is removed from the liquid phase by freezing.

3. The main factors causing salinity variations are climatic; lake and catchment morphometry may modify such effects. These influences have been poorly quantified.

4. The pH of a water normally rises during the summer period; this is attributed to biological activity.

5. pH varies diurnally: there is normally a rise during the light period and a fall during the night.

6. The diurnal pH range is greatest during the summer.

7. Stoichiometry of saline water solutions is almost invariable; temporary waters are more variable than permanent ones.

8. Stoichiometric variability of fresh waters is generally greater than for saline waters; catchment contributions are most pronounced during the wet period.

9. The first inflows after a dry period may cause a reduction of pH,

increase of colour, a stoichiometric displacement towards seawater and increases in the concentrations of many dissolved species, including the nutrients; these changes represent the flushing of materials from the catchment.

10. Variability of stoichiometry is a function of weather variability, and morphometric features of the water body and the catchment; sediments may exert a buffering influence.

11. Biological activity may significantly alter the chemical behaviour of a water, particularly in regard to alkalinity, organic matter and nutrients.

12. The literature evidences a disjointed approach to an identification and description of the features of chemical changes in inland waters.

CHAPTER 11

THE GENERAL FEATURES OF INLAND WATER CHEMISTRY, AND AN INVESTIGATION OF THE APPLICABILITY OF THE BINARY NOTATION: (CONCENTRATION, STOICHIOMETRIC DISTANCE) TO THE MAJOR ION CHEMISTRY OF TASMANIAN INLAND WATERS.

CONTENTS

1. ABSTRACT

The major features of inland waters and the factors controlling their major ion composition are discussed. Some aspects of the problem of convenient numerical representation of major ion chemistry are discussed and a simple binary notation adopted to describe the chemistry of inland waters.

The applicability of the binary notation to a description of Tasmanian inland waters is investigated. Some conclusions regarding possible equilibrium states and controls on pH are discussed.

Some inferences concerning the chemical variability of single waters are made.

2. SUMMARY OF PRIMARY CONTROLS ON WATER CHEMISTRY

Gibbs (1970) showed the importance of the three factors:

(1) the supply of ions from the atmosphere,

(2) the accession of dissolved material from rocks, and

(3) the evaporative concentration of the solutions formed in establishing the chemical character of a water. In the previous chapter biotic influences were identified as important factors affecting the variation of water chemistry in single waters; the bulk of this chapter deals with the usefulness of a modification of Gibbs' numerical notation in describing water chemistry. The basic reasoning of Gibbs(1970) is retained, so that the chemistry of a water is viewed as being determined largely by the three factors listed above.

Climate may influence the supply of ions from the atmosphere and the rate of weathering of rock, but its main effect is to determine the concentrations of ions in solution by evaporation; the most saline surface-fed waters are restricted to arid areas (Langbein, 1961). At very high concentrations the solubilities of some salts - particularly of calcium and magnesium - often limits the concentrations of these ions. This results in the preponderance of saline waters with a major ion stoichiometry similar to seawater (Buckney and Tyler, unpublished*; Gibbs, 1970). Solutions of different stoichiometry may be found at very high concentrations (Kilham, 1971).

Atmospheric supply of ions is the least possible ion supply for any one location. In the absence of other influences surface water chemistry is the same as that of the rainfall. This is stoichiometrically like seawater in coastal or insular situations (Buckney and Tyler, 1973a, 1974; Gorham, 1958, 1961; Tyler, 1972); inland, calcium and other elements from terrestrial dust may be significant in rainwater (Hutton and Leslie, 1958; Miller, 1961).

* See appendix for summary.

Geological contributions to inland waters are as variable as the rock type. Many igneous and metamorphic rocks contribute only little to the dissolved material of waters draining them (Gorham, 1961), while many volcanic rocks, limestones, dolomites and their derivatives are quite soluble in the weakly acidic solutions of rainwater, forming solutions of (mainly) alkaline earth bicarbonates (Gorham, 1961; Holmes, 1965). Thus, the geological component of the influences acting on inland waters most markedly affects the ionic dominance of the waters. Clearly, geologically - derived substances will also contribute to the total concentration of inland waters by simple addition of dissolved material.

3. APPROACH TO THE PROBLEM OF CHEMICAL REPRESENTATION

To specify the major ion chemistry of a water, it is sufficient to record the total concentration and the relative proportions of the major ions. These express respectively the importance of climate and of geological contributions in modifying the chemical character of the local rainwater. If the seven ions Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} and HCO_3^- are considered, then the specification of chemical character would require the nomination of at least five figures, four of which would refer to the stoichiometry of the solution. Because these figures convey some information about conditions prevailing in the catchment, it is possible that they - as a whole - can be shown to be related to other chemical features of the water in question. That is, it is possible that the total concentration and stoichiometry specify, to some extent, other parameters - such as pH, Si concentration etc. - that are similarly determined by catchment conditions. Clearly, if this is the case, the discussion and investigation of chemical conditions in waters could be simplified. The use of five figures would be prohibitive, and a single figure denoting the stoichiometry of the water would be desirable.

The following paragraphs explore the terms which may be used or derived to construct a simplified binary notation for the specification of the chemical character of a water.

(A) CONCENTRATION

The total quantity of dissolved material may be represented by any of a number of parameters of the 'global' or 'integrative' type (Dussart 1967). These include measures of total dissolved solids (TDS), conductivity, salinity and equivalent concentration. All of these are related.

For practical reasons, the use of T.D.S. may be considered unsatisfactory. Conductivity determination is relatively simple.

The use of salinity (= sum of ion concentrations in weight units per unit volume) and of total equivalent concentration (= sum of ion concentrations in equivalents per unit volume) has been found convenient for this study, since both may be determined by addition from the routine analysis of a water. For reasons of analytical confidence, the total cation equivalent concentration, Σ^+, has been used to represent total equivalent concentration (Σ^+ is approximately equal to half the total ionic concentration). Further, it has been found convenient to use $\log \Sigma^+$ (Σ^+ in μ equ. l^{-1}) when dealing with a large range of concentrations.

Σ^+ in μ equ. l^{-1} is related to salinity, S, in p.p.m. by the regression equation:

$$\log S = 0.962 \log \Sigma^+ - 1.046; \; r = 0.999, \; n > 300.$$

(B) STOICHIOMETRY

Any parameter which is a function of the ionic proportions of all ions present may be used to represent the stoichiometry of a water.

Many of the 'global' parameters (Dussart, 1967) can be shown to be a function of the proportions of the dissolved substances present. If such a 'global' figure is reduced to unit equivalent concentration, then some information is conveyed about the stoichiometry of the water. Two examples follow:

(i) The Ratio $\frac{K18}{\Sigma^+}$

The relative composition of a water is related to its conductivity,

K18, as follows.

$K18 = \sum (c)_x k_x$ where $(c)_x$ is the equivalent concentration of ion X, and k_x is its equivalent conductivity at $18^{o}C$ i.e.,

$$K18 = k_{Na}(Na) + k_K(K) + k_{Ca}(Ca) + k_{Mg}(Mg) + k_{Cl}(Cl) + k_{SO_4}(SO_4) + k_{HCO_3}(HCO_3)$$

for a water in which only the specified ions contribute to conductivity; most dilute, oligotrophic unpolluted waters will approximate to this condition. Since $\Sigma^+ = \Sigma^-$,

$$\frac{K18}{\Sigma^+} = k_{Na'}\,Na + k_{K'}\,K + K_{Ca'}\,Ca + k_{Mg'}\,Mg + K_{Cl'}\,Cl + k_{SO_4'}\,SO_4 + k_{HCO_3'}\,HCO_3$$

, where Na, K, Ca, Mg, Cl, SO_4, HCO_3, are the equivalent proportions of the respective ions in solution, expressed as proportions of total cation or anion concentrations.

Using matrix notation, this reduces to the linear transformation:

$$\left[\frac{K18}{\Sigma^+}\right] = \left[k_{Na}\ k_K\ k_{Ca}\ k_{Mg}\ k_{Cl}\ k_{SO_4}\ k_{HCO_3}\right] \begin{bmatrix} Na \\ K \\ Ca \\ Mg \\ Cl \\ SO_4 \\ HCO_3 \end{bmatrix} = \left[K\right]\left[c\right],$$

where the vector $\left[K\right]$ is a constant.

Thus, relative ionic composition (stoichiometry) of a water may be expressed by the ratio $\frac{K18}{\Sigma^+}$. In theory, there is no limit to the ions which may be included in the vector $\left[c\right]$, but as stated above, the seven nominated ions would probably be adequate for most purposes. It may be necessary to incorporate the hydrogen ion into $\left[c\right]$ for some acidic waters.

The ratio $\frac{K18}{\Sigma^+}$ does not permit an immediate knowledge of stoichiometry; however, since the elements of $\left[K\right]$ are constants the ratio varies in a definable manner with $\left[c\right]$.

(ii) The ratio $\frac{\text{Salinity}}{\Sigma^+}$, $\frac{S}{\Sigma^+}$

In the same way, this ratio reduces to a linear transformation in which the constant vector is the array of equivalent weights.

The ratio $\frac{K18}{\Sigma^+}$ is probably sufficiently variable (range in this study from ca. 0.5 to ca. 1.3) to be useful. However there are many substances which may contribute to K18 but which are not normally (nor easily) determined in a routine analysis of a water; organic substances are probably the most notable of these, though in some saline waters certain inorganic ions can be included among these.

The ratio $\frac{K18}{\Sigma^+}$ may be applicable to certain problems related to the physiology of planktonic organisms, since it conveys information about the electrical properties of the "mean ion" in solution.

The ratio $\frac{S}{\Sigma^+}$ is probably too invariable to be of much use, but since S can be calculated using just the concentrations of ions used in calculating Σ^+, it would be more useful than $\frac{K18}{\Sigma^+}$ over a wide salinity range.

Another approach to the representation of stoichiometry is to derive a parameter from the known ionic proportions. This approach is a somewhat more laborious one, but has the advantage of providing a greater measure of flexibility than the peceeding parameters. A derivation follows.

(iii) Stoichiometric Distance

The set of seven ionic concentrations which define the major ion chemistry of most waters may be viewed as the coordinates defining the position of a point in a seven-dimensional space. The seven relative ionic proportions which define the stoichiometry of the water similarly may be viewed in the context of a seven-dimensional space. It is not difficult to combine these seven figures to form a single number which represents the distance in the hyperspace between an origin point (origin stoichiometry) and the point specifying the water's stoichiometry.

Let $d^{\pm}$ be the distance between the origin point: (Na_o, K_o, Ca_o, Mg_o, Cl_o, SO_{4_o}, HCO_{3_o}) and the point: (Na, K, Ca, Mg, Cl, SO_4, HCO_3) specifying the

Stoichiometry of the water. Then:

$$(d^{\pm})^2 = (Na - Na_o)^2 + (K - K_o)^2 + (Ca - Ca_o)^2 + (Mg - Mg_o)^2 + (Cl - Cl_o)^2 + (SO_4 - SO_{4_o})^2 + (HCO_3 - HCO_{3_o})^2$$

$$\text{i.e., } d^{\pm} = \sqrt{(Na - Na_o)^2 + (K - K_o)^2 + (Ca - Ca_o)^2 + (Mg - Mg_o)^2 + (Cl - Cl_o)^2 + (SO_4 - SO_{4_o})^2 + (HCO_3 - HCO_{3_o})^2}$$

The origin point may be selected arbitrarily. A few compositions might be found relevant:

(a) Pure Water. This is the true origin of the seven-dimentional system. The terms Na_o, K_o, Ca_o, Mg_o, Cl_o, SO_{4_o}, HCO_{3_o} are each zero.

(b) Sea Water. This is the empirical composition of the "minimum supply" inland waters; the terms Na_o, K_o, Ca_o, Mg_o, Cl_o, SO_{4_o}, HCO_{3_o} are respectively: 0.772, 0.016, 0.034, 0.178, 0.903, 0.093, and 0.004.

(c) World Average Freshwater. (Livingstone, 1963). The terms are respectively: 0.157, 0.034, 0.635, 0.174, 0.101, 0.160, 0.739.

The range of variation of the proportions is not the same for all elements. In Tasmania, for example, it is least for potassium and greatest for chloride. For this reason it is desirable, when using distance to elucidate features of a spectrum of waters, that for a water which (in absolute terms) is displaced from the K origin, K_o, by the same amount as from the Cl origin, Cl_o, the distance incorporates the K displacement as a larger proportion than the Cl displacement. That is, the K displacement ought to be "weighted" to contribute proportionately more to distance than the Cl displacement. Similarly, the other ions should be weighted by factors which are inversely proportional to the empirical range of their relative proportions.

Following the practice of Sokal (1961) weighted distance, $D^{\pm}$ is defined by the equation:

$$D^{\pm} = \sqrt{\frac{(Na - Na_o)^2}{V_{Na}} + \frac{(K - K_o)^2}{V_K} + \frac{(Ca - Ca_o)^2}{V_{Ca}} + \frac{(Mg - Mg_o)^2}{V_{Mg}} + \frac{(Cl - Cl_o)^2}{V_{Cl}} + \frac{(SO_4 - SO_{4_o})^2}{V_{SO_4}} + \frac{(HCO_3 - HCO_{3_o})^2}{V_{HCO_3}}}$$

, where V_x is the variance of the proportion of ion X among all waters considered. More sophisticated controls may be applied to $D^{\pm}$. For example it is possible to minimise the contributions to $D^{\pm}$ by ion pairs whose concentrations vary in the same way. Among the Tasmanian waters (Buckney and Tyler, 1973a), sodium and chloride concentrations are statistically related; compensation for covariance in such situations has not been attempted in this treatment.

An estimate of the value of $D^{\pm}$ can be obtained from the cation distance, D^+, or anion distance, D^-, calculated respectively from cation and anion proportions only. For Tasmanian waters:

$$D^+ = 0.773\, D^{\pm} - 0.136; \quad r = 0.867, \quad D^+ \ll D^{\pm}$$

$$D^- = 0.618\, D^{\pm} + 0.054; \quad r = 0.696, \quad D^- \ll D^{\pm}$$

In general terms, $D^{\pm}$ is high when geochemical influences are high; that is, when calcium, bicarbonate (and to a lesser extent magnesium and potassium) proportions are high in the water.

The following sections are a report on a treatment of the chemistry of Tasmanian inland waters which uses the binary notation: (concentration, stoichiometry) as the only means to describe the major ion chemistry. The specific notation used is $(\log \Sigma^+, D^{\pm})$. The weighting factors used in the calculation of $D^{\pm}$ are the variances of the relative proportions of the major ions found for all Tasmanian waters analysed. The major features of Tasmanian waters have been published (Buckney and Tyler, 1973a); more recent analyses have been included in the treatment below. The total number of samples is 334.

The purpose of the following section is to determine (a) whether the binary notation used allows an interpretation of the survey chemistry which is in keeping with the results obtained by the more conventional means and (b) how

far the notation is definitive of chemical parameters which do not contribute to either Σ^+ or $D^{\pm}$. Thus, the following section provides an indication of the limits which apply to some aspects of the discussion of chemical variability in the following chapters.

4. APPLICABILITY OF THE BINARY NOTATION: ($\log\Sigma^+$, $D^{\pm}$) TO THE CHEMISTRY OF TASMANIAN INLAND WATERS

(A) TASMANIAN WATERS AS A WHOLE

(i) General Features

The distribution of $D^{\pm}$ over the range of concentration found for Tasmania is shown in Fig. 11.1. Values of $D^{\pm}$ range from near zero to about 10; values of $\log\Sigma^+$ range from about 2 (S = 10 p.p.m.) to about 7 (S = 200‰). The range of $D^{\pm}$ is greatest at low values of $\log\Sigma^+$; there is a progressive reduction in the range of $D^{\pm}$ from $\log\Sigma^+$ = ca. 4 (S = 1‰) to $\log\Sigma^+$ = ca 5.3 (S = 11‰). This is in agreement with the observation by Buckney and Tyler (Unpublished*) that the expression of a geochemical influence on waters is decreased at higher concentrations, and with the observations by others (Bayly and Williams, 1966; Kilham, 1971; Langbein, 1961; Williams, et al., 1970) that saline waters tend to have a stoichiometry similar to that of sea water. More specific observations such as the restriction of a near sea water stoichiometry in dilute waters to inert rocks (Buckney and Tyler, 1973a), is confirmed by the data relating to $\log\Sigma^+$ and $D^{\pm}$; the detailed discussion of this is not included here.

(ii) Specification of pH by the notation used.

(a) General Features

Figure 11.2 shows the overall relation between pH, $D^{\pm}$ and $\log\Sigma^+$. A few major features can be discerned: The range of pH is least at high values of $D^{\pm}$. That is, a geological influence is expressed by the attainment of a

* See appendix for summary

FIGURE 11.1 : THE DISTRIBUTION OF D_{-}^{+} OVER THE CONCENTRATION RANGE OBSERVED FOR TASMANIAN WATERS.

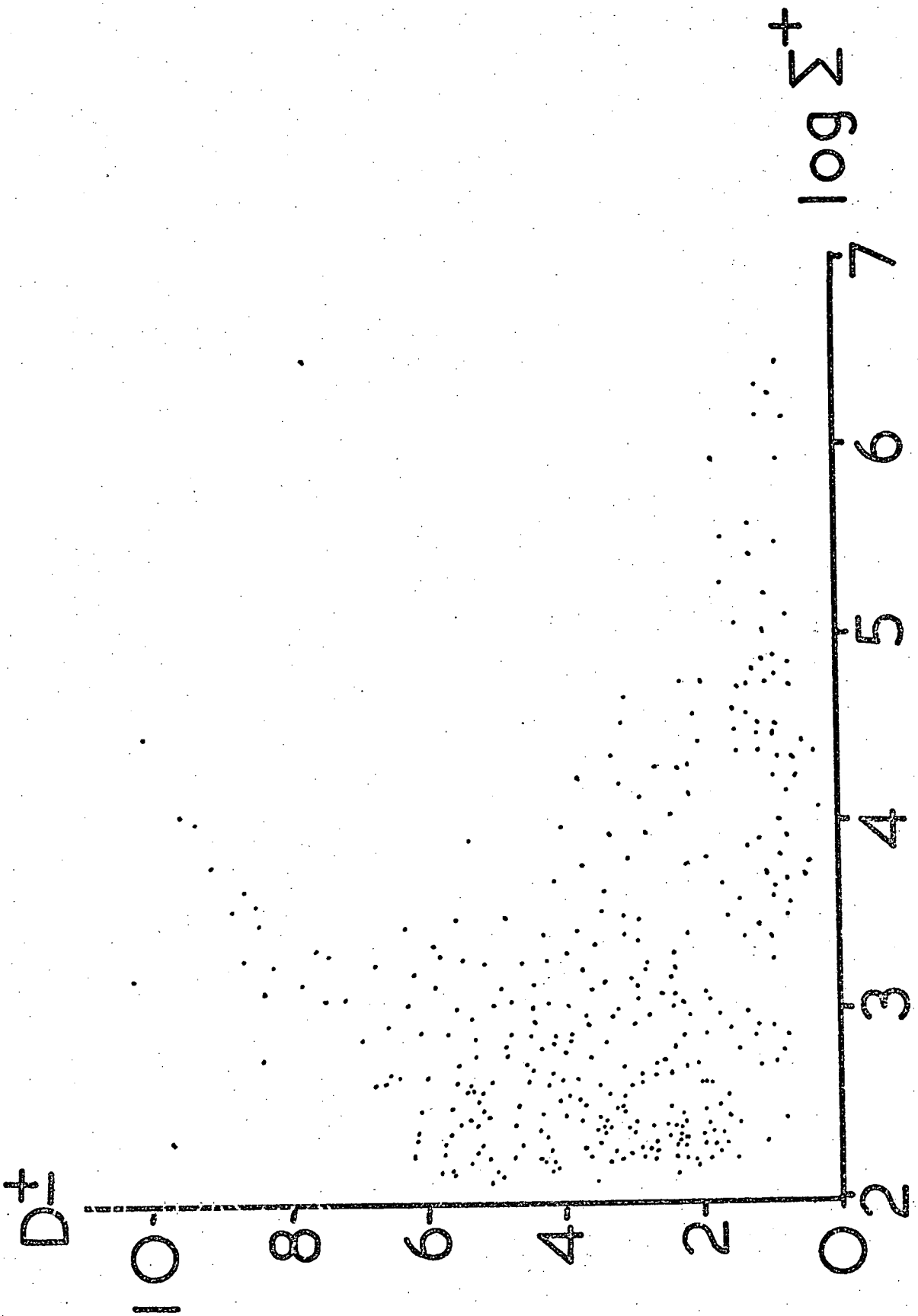
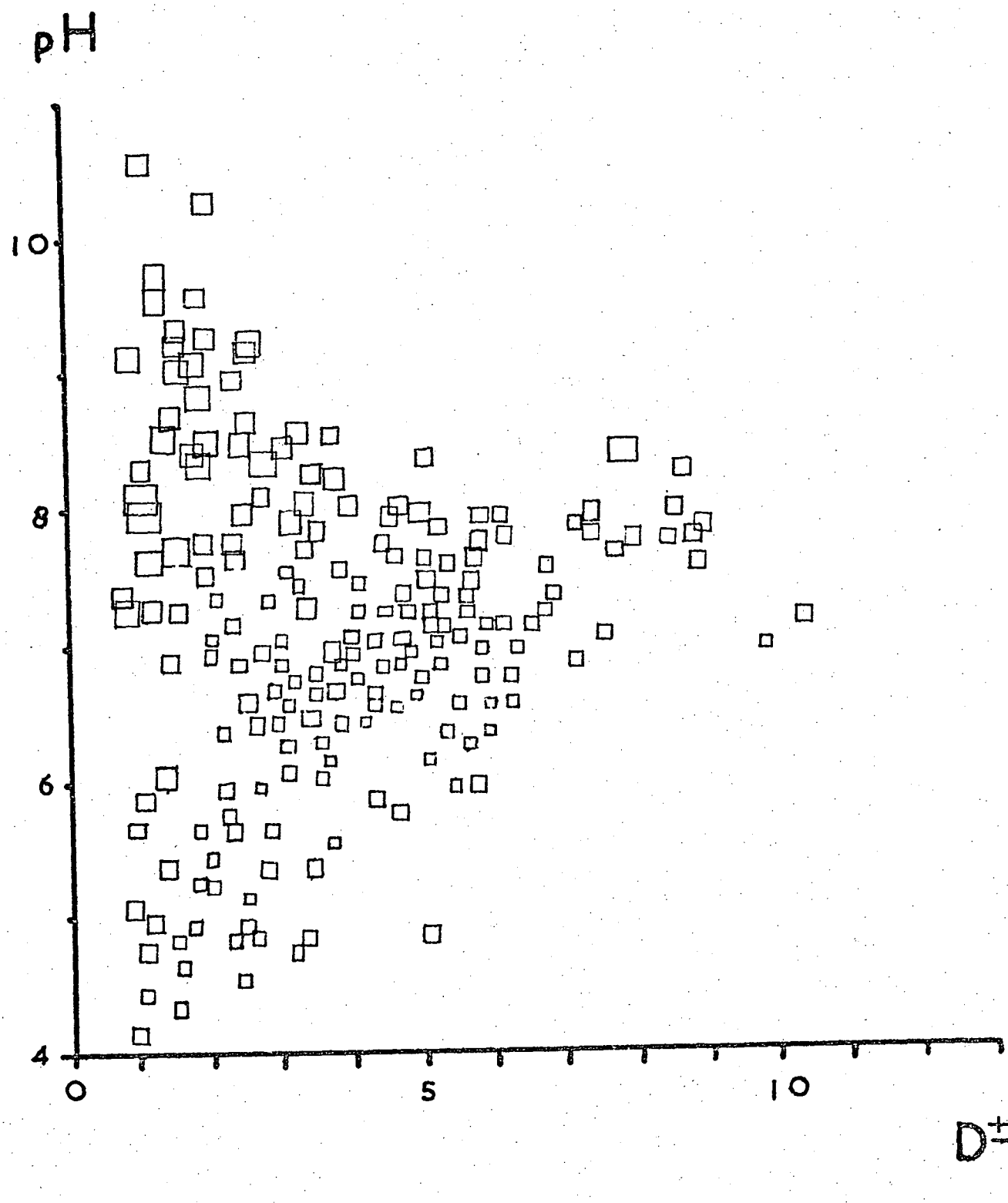

$\log M_{\odot}$
7
6
5
4
3
2
$D_{\odot}^{+1}$
0
8
6
4
2
0

FIGURE 11.2 : THE RELATION BETWEEN pH, $D^{\pm}$ AND CONCENTRATION FOR TASMANIAN WATERS.

THE SIZE OF EACH SQUARE IS PROPORTIONAL TO LOG Σ^{+}.

(Some points omitted to avoid excessive overlap.)


pH
10
8
6
4
0
5
10
D±

distinct pH value; this argues for the existence of a specific equilibrium which determines pH in waters experiencing a geological influence. This may be the Ca - CO_3 equilibrium system (Morton and Lee, 1968).

Among the waters with a near-seawater stoichiometry ($D^{\pm}$ small) a high pH is attained only when total concentration is high; the most saline waters do not however have the highest pH values. Figure 11.3 is a plot of pH against $\log \Sigma^+$ for waters of near-seawater stoichiometry ($D^{\pm}$ 1.5). Clearly, it is possible to identify a concentration ($\log \Sigma^+$ = ca. 5.2) at which a maximum pH (10.3) is attained. This is about the same total concentration at which the progressive restriction of the range of $D^{\pm}$ ceases (see Fig. 11.1), and proposed (Buckney and Tyler, unpublished*) as the upper concentration limit to the "fresh" waters.

(b) Statistical

If the entire ranges of $D^{\pm}$ and $\log \Sigma^+$ are partitioned into contiguous subunits, the surface defined by these two parameters may be subdivided into a number of smaller rectangular units. The waters which are defined in terms of $D^{\pm}$ and $\log \Sigma^+$ may then be considered in groups; all waters within one of these groups are similar with respect to $D^{\pm}$ and $\log \Sigma^+$, the extent of the similarity being a function of the sizes of the partition subunits. The degree to which $D^{\pm}$ and $\log \Sigma^+$ define the pH of the waters may be guaged from the mean and standard deviation of the pH of those waters within each group. Figure 11.4 summarises the data of $D^{\pm}$, $\log \Sigma^+$ and pH in this way. The ranges of $D^{\pm}$ and $\log \Sigma^+$ have been partitioned in a way which as far as possible subdivides the $D^{\pm}$ - $\log \Sigma^+$ surface equally. Where the number of waters sampled is small in a group, the group has been enlarged to incorporate more samples; a minimum sample number of 5 has been used, but for most of the dilute waters, the number of samples in a group is greater than 15.

The standard deviations of the pH values for the grouped waters range from

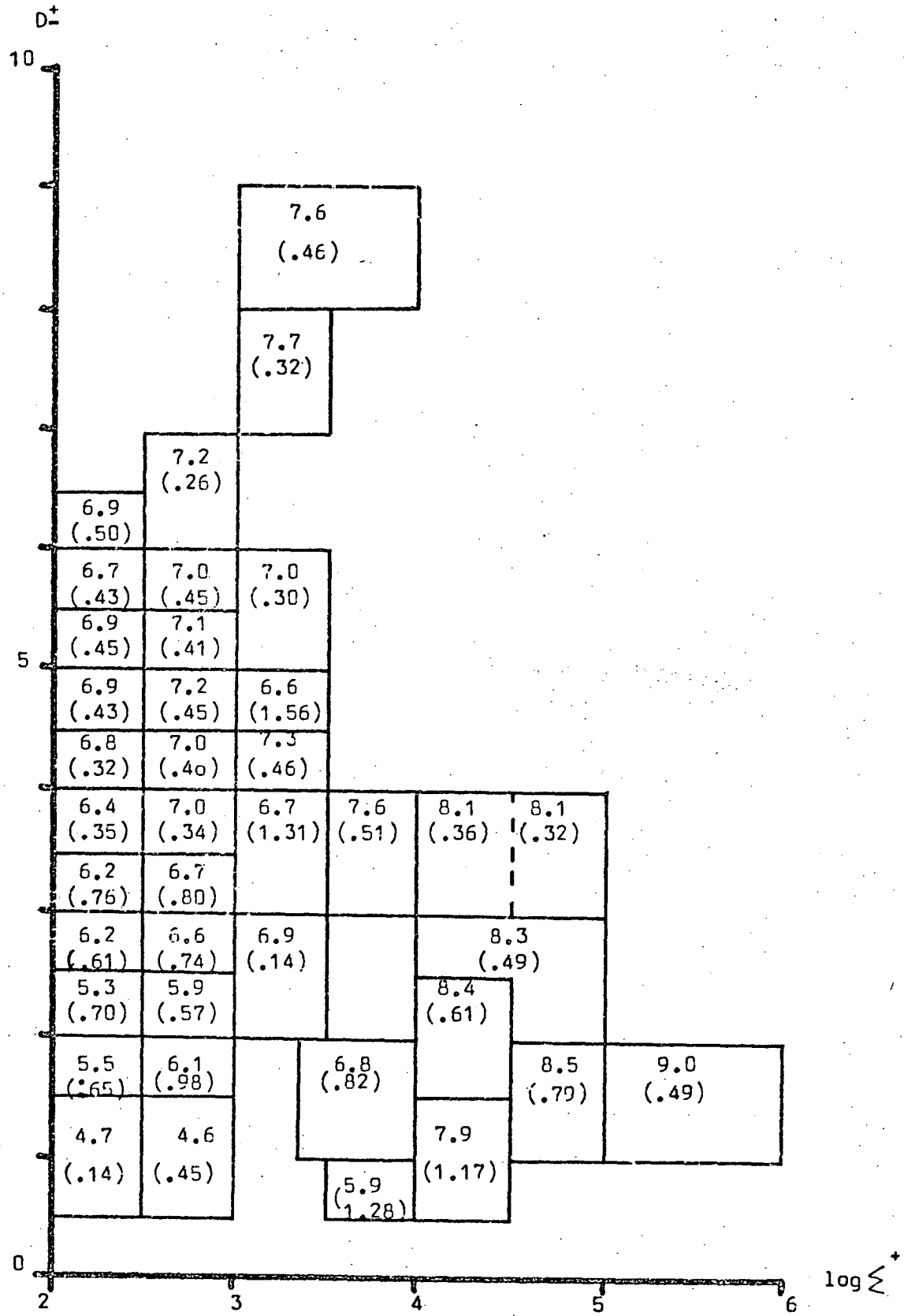
* See appendix for summary

FIGURE 11.3 : VARIATION OF pH WITH CONCENTRATION FOR WATERS OF NEAR-SEAWATER STOICHIOMETRY ($D^{\pm} < 1.5$).

S = Seawater.

log Σ+
2
3
4
5
6
pH
10
9
8
7
6
5
4
S

FIGURE 11.4 : MEANS AND (IN PARENTHESES) STANDARD DEVIATIONS OF pH OF WATERS GROUPED ACCORDING TO CONCENTRATION AND STOICHIOMETRY.



0.14 to 1.56. Definition of pH is best (standard deviation lowest) among the most dilute waters with low $D^{\pm}$; pH is least well defined among waters of pH between about 6 and 7. The standard errors of pH are less than 5% of the group means in 35 of the 40 groupings employed, the largest standard error being 13.7% of the mean.

The precision with which pH is defined by stoichiometry and total ionic concentration is sufficiently great to hint at a major-ion control on pH, particularly for the dilute acid waters. Sillen (1961) and Wangersky (1972) have assigned significance respectively to the major ion chemistry and to ion pairing in determining the pH of seawater, though such effects may be unimportant in fresh waters.

(iii) Specification of SiO_2 concentration by the notation used.

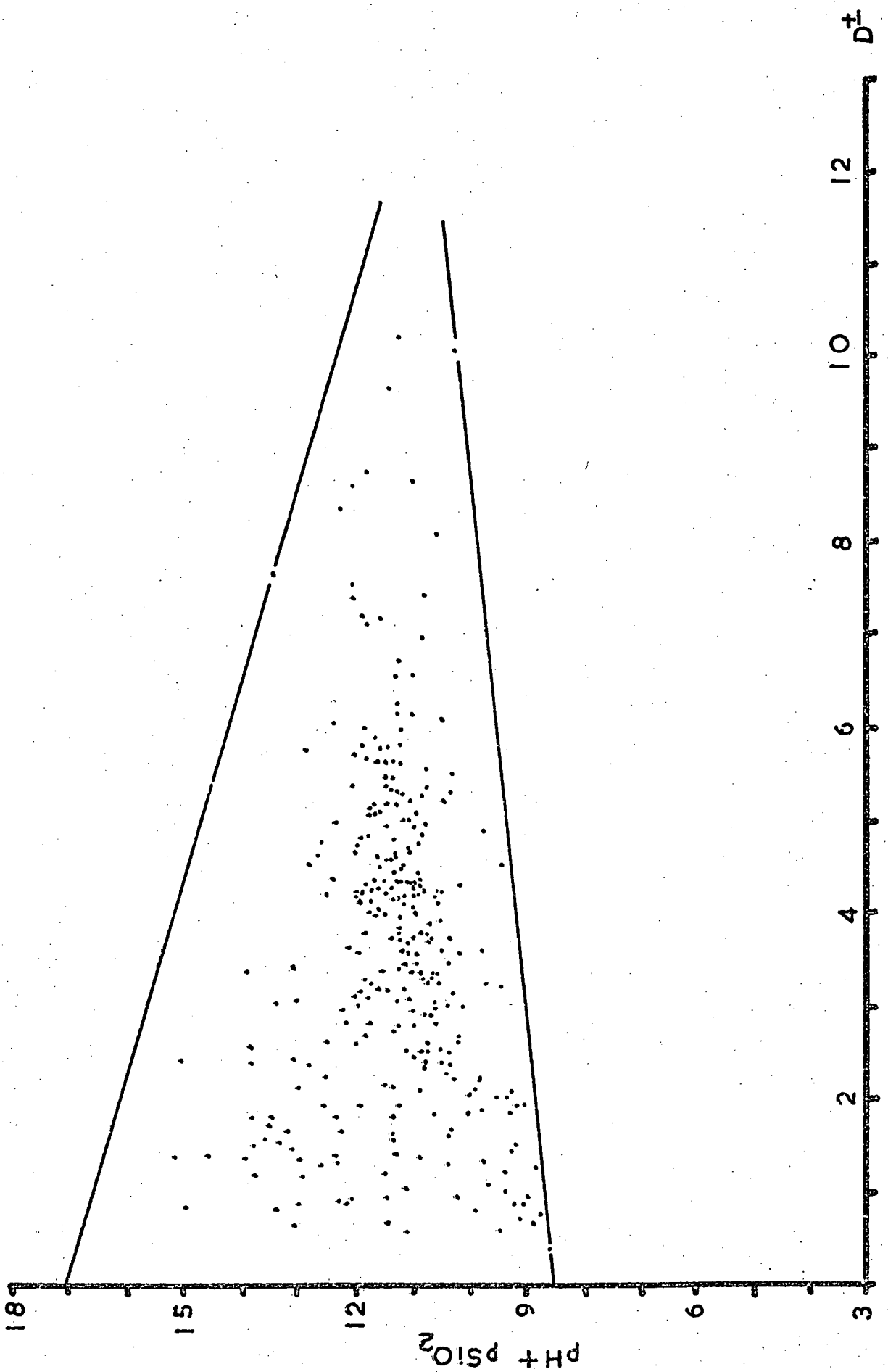
(a) General

As for pH, there has not been found any significant regression of SiO_2 concentration on Σ^+ or $D^{\pm}$. Figure 11.5 shows the plot of $(pH + pSiO_2)$ against $D^{\pm}$ for most waters sampled, and provides evidence of a tendency for silica concentration to be high when pH is high in geochemically-influenced waters. The lines in Fig. 11.5 illustrate the approximate limits of $(pH + pSiO_2)$. That is, $8.5 + 0.19D^{\pm} < (pH + pSiO_2) < 17 - 0.47D^{\pm}$. The distribution is less dispersed than this over much of the range of $D^{\pm}$, while at low values of $D^{\pm}$, $pSiO_2$ can be very high (SiO_2 concentrations undetectable); these latter points have been omitted from Fig. 11.5.

At high values of $D^{\pm}$ the range of $(pH + pSiO_2)$ is markedly limited in comparison to the range found for lower values of $D^{\pm}$. This suggests that in geologically-influenced waters, a defined value of $(pH + pSiO_2)$ is attained, suggesting that an equilibrium situation exists. Tessenow (1966) has discussed the importance of pH-dependent equilibria in determining silica concentrations

FIGURE 11.5 : THE DISTRIBUTION OF ($pH + pSiO_2$) OVER THE OBSERVED RANGE OF $D^{\pm}$.

Waters with SiO_2 undetectable, ($D^{\pm} <$ about 2) omitted.


D^{+}
2
4
6
8
10
12
3
6
9
12
15
18
$pH + pSiO_2$

in inland waters.

At lower values of $D^{\pm}$ it is possible that several influences operate to control the solubility of silica; the dissociation of silica complexes of (for example) iron and aluminium may contribute (Hutchinson, 1957).

(b) Statistical

Figure 11.6 summarises the distribution of SiO_2 concentrations and the standard errors of the samples grouped as for pH. Standard errors range from 12.1% to 88.6% of the means. It is obvious that silicon concentrations is less well defined by $D^{\pm}$ and $\log\Sigma^+$ than pH, in the sense that the standard errors of the SiO_2 concentrations for the grouped samples are substantially higher than those for pH. Definition is best for $\log\Sigma^+ < 2.5$ and $D^{\pm}$ between 3 and 4; that is, for the most dilute waters with moderate geochemical influence.

(iv) Iron Concentration

(a) General

Iron determinations were not made on all waters, so the data for this element are not as useful as those for other parameters. Some features can be noted, however.

Figure 11.7 shows the relation between $D^{\pm}$, $\log\Sigma^+$ and iron concentration. Clearly, high iron concentrations are more common at values of $D^{\pm}$ less than about 5. The highest concentrations are found at values of $\log\Sigma^+$ between 3 and 4; the very high value obtained for one saline water may simply be due to non atomic absorption in the determination of iron for this water. There are inadequate data to formulate any generalities about iron concentrations in saline waters.

In general terms, the findings do not contradict the observation by Buckney and Tyler (1973a) that high iron concentrations are common in humic, acid waters with a near-seawater stoichiometry.

(b) Statistical

Figure 11.8 presents the mean values of iron concentrations for the

FIGURE 11.6 : MEANS AND (IN PARENTHESES) STANDARD ERRORS AS PERCENTAGES OF THE MEANS OF SiO_2 CONCENTRATIONS FOR WATERS GROUPED ACCORDING TO TOTAL CONCENTRATION AND STOICHIOMETRY.

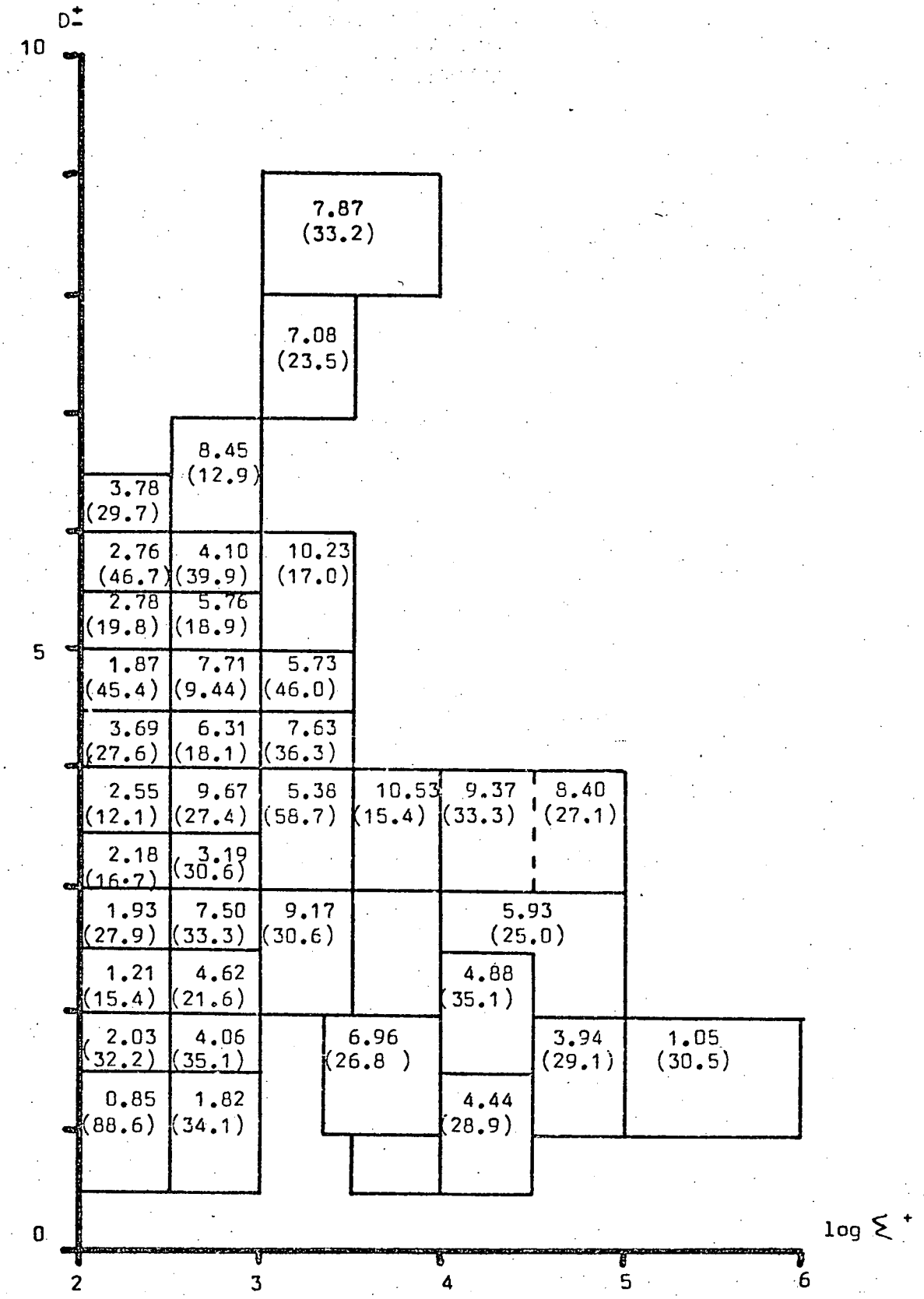


FIGURE 11.7 : RELATION BETWEEN IRON CONCENTRATION, $D^{\pm}$ AND TOTAL CONCENTRATION FOR TASMANIAN WATERS. THE SIZE OF EACH SQUARE IS PROPORTIONAL TO THE IRON CONCENTRATION.

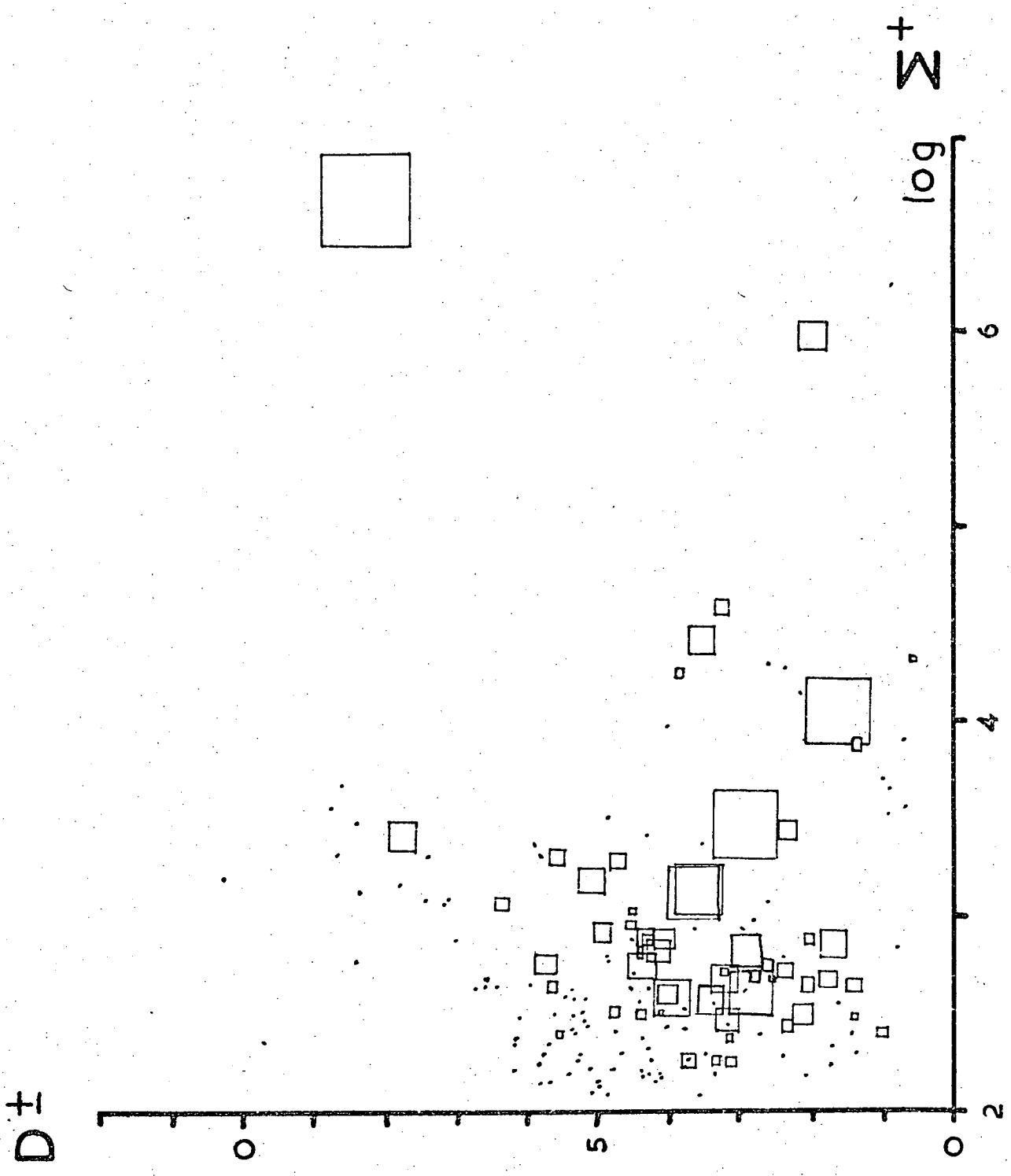
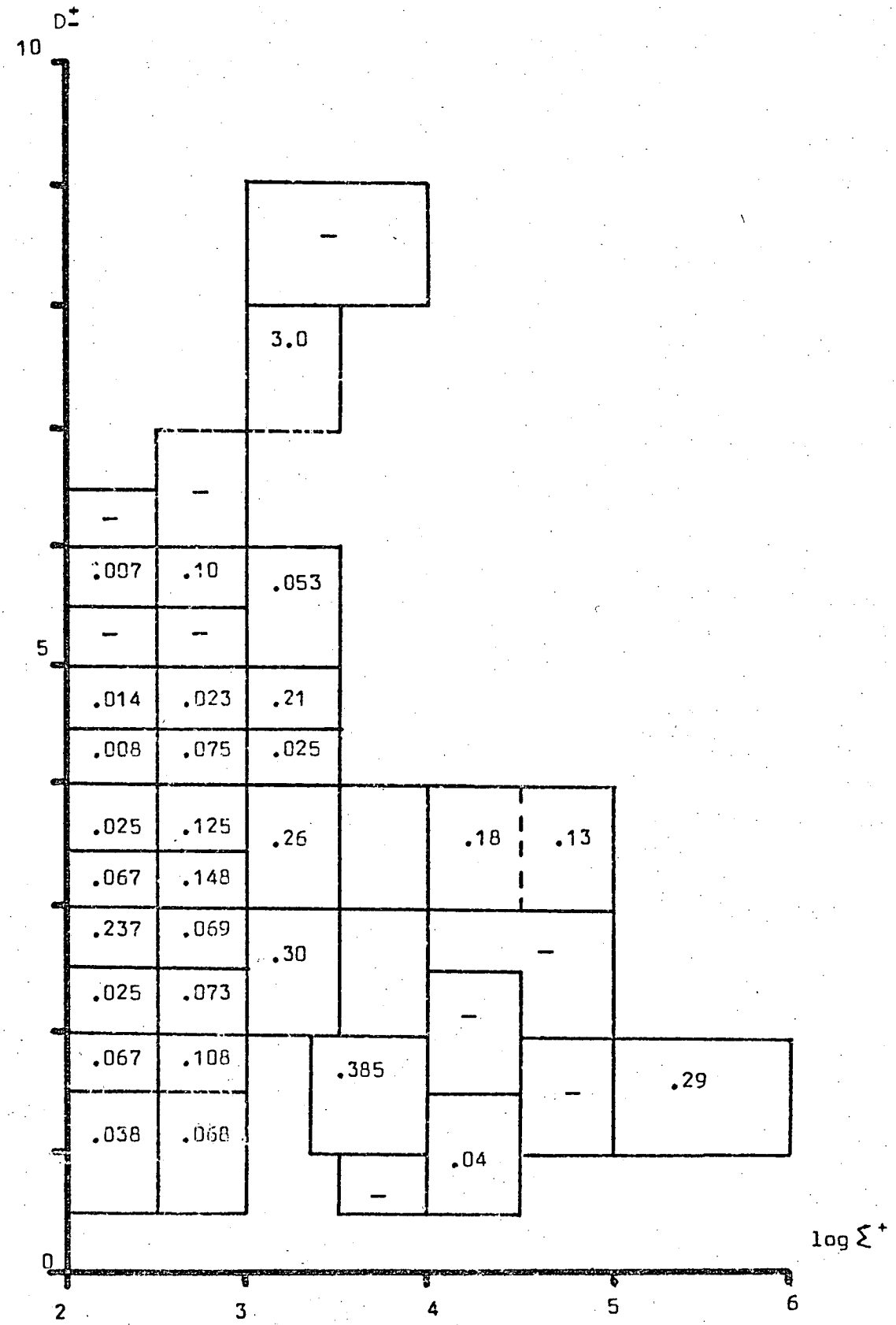

M+
log
6
4
2
0
5
0
D+
0

FIGURE 11.8 : MEANS OF IRON CONCENTRATIONS FOR WATERS GROUPED ACCORDING TO TOTAL CONCENTRATION AND STOICHIOMETRY.

- indicates undetectable.



waters sampled in groups. In the absence of large numbers of samples, the standard errors of the groups have not been presented, but for the most part standard errors are quite low at high values of D^{+}_{-}. That is, iron concentration appears to be most invariant among the geochemically-affected waters where it is also lowest.

(v) Specification of Colour Intensity

(a) General

Figure 11.9 represents the distribution of colour values over the range of D^{+}_{-} and $\log\Sigma^{+}$. Clearly, the data indicate that waters displaying a geochemical influence (D^{+}_{-} high) are the least coloured. This is in keeping with earlier findings (Buckney and Tyler, 1973a).

(b) Statistical

Colour measurements were made using glass disc standards causing the smallest discernible colour difference to be 5 Hazen units at low colour values, and the largest difference to be 50 units at high values (colour $\geqslant$ 100). Figure 11.10 summarises the means and standard deviations of the colour values for the grouped waters, and indicates that the definition of colour by D^{+}_{-} and $\log\Sigma^{+}$ is relatively precise, bearing in mind the discontinuous nature of the colour scale. Definition of colour would seem to be best at high values of D^{+}_{-} and at high values of $\log\Sigma^{+}$ where the absolute values of colour are low.

(vi) Turbidity

There is no *a priori* reason to suspect that turbidity is subject to the same sorts of controls as dissolved substances, but since D^{+}_{-} is representative of the extent of a geological influence and $\log\Sigma^{+}$ of a climatic influence, then an investigation of the variation of turbidity over the ranges of D^{+}_{-} and $\log\Sigma^{+}$ might illuminate some features regarding the nature of suspended material.

In the absence of an adequate number of samples for which turbidity estimates are available, the data allow only tentative observations to be made here. Figure 11.11 summarises the relation between group means, D^{+}_{-} and $\log\Sigma^{+}$.

FIGURE 11,9 : THE RELATION BETWEEN COLOUR, $D^{\pm}$ AND TOTAL CONCENTRATION FOR TASMANIAN WATERS. THE SIZE OF EACH SQUARE IS PROPORTIONAL TO THE COLOUR.

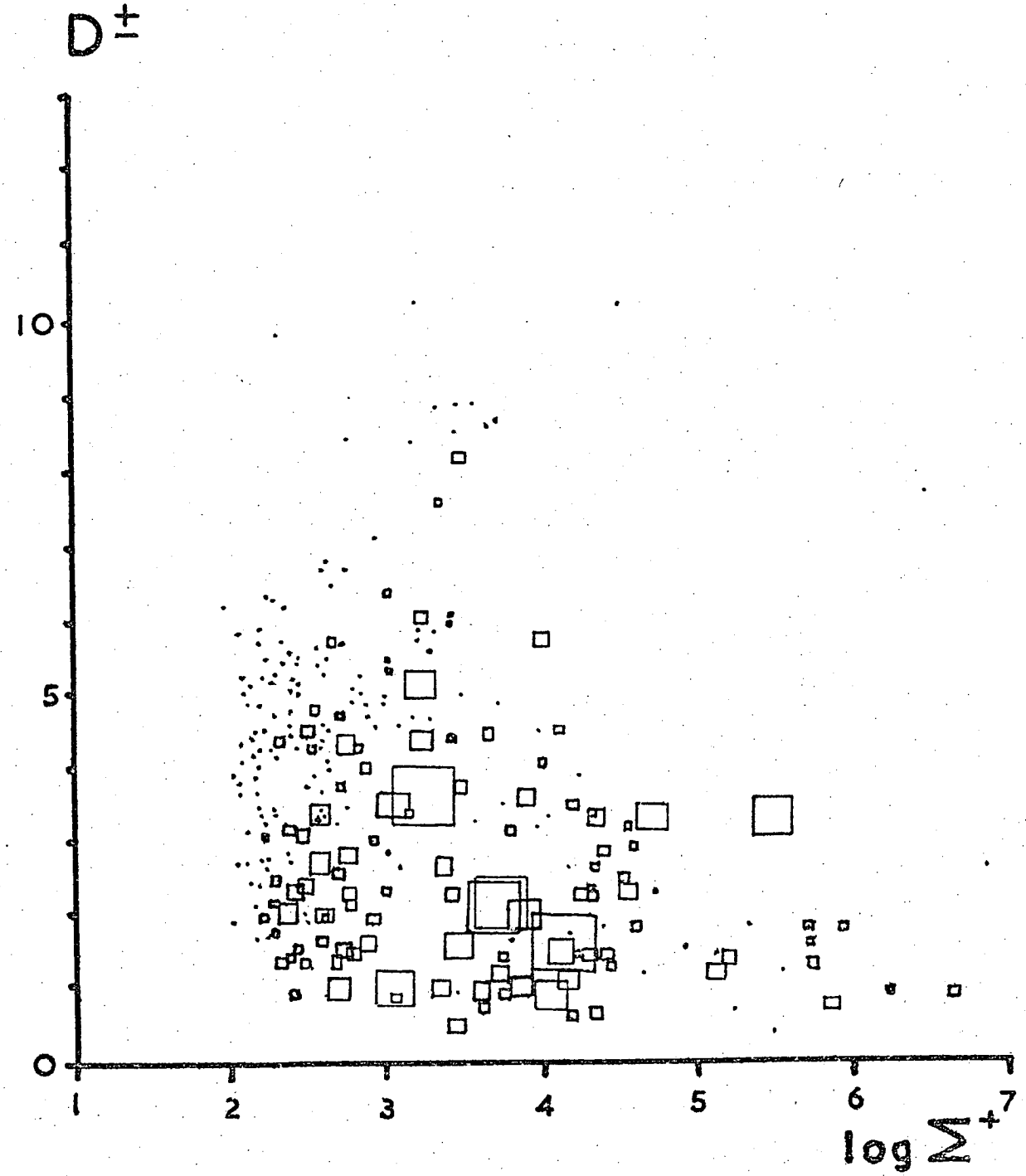

D±
10
5
0
1
2
3
4
5
6
7
log Σ+

FIGURE 11.10 : MEANS AND (IN PARENTHESES) STANDARD DEVIATIONS OF COLOUR FOR WATERS GROUPED ACCORDING TO TOTAL CONCENTRATION AND STOICHIOMETRY.

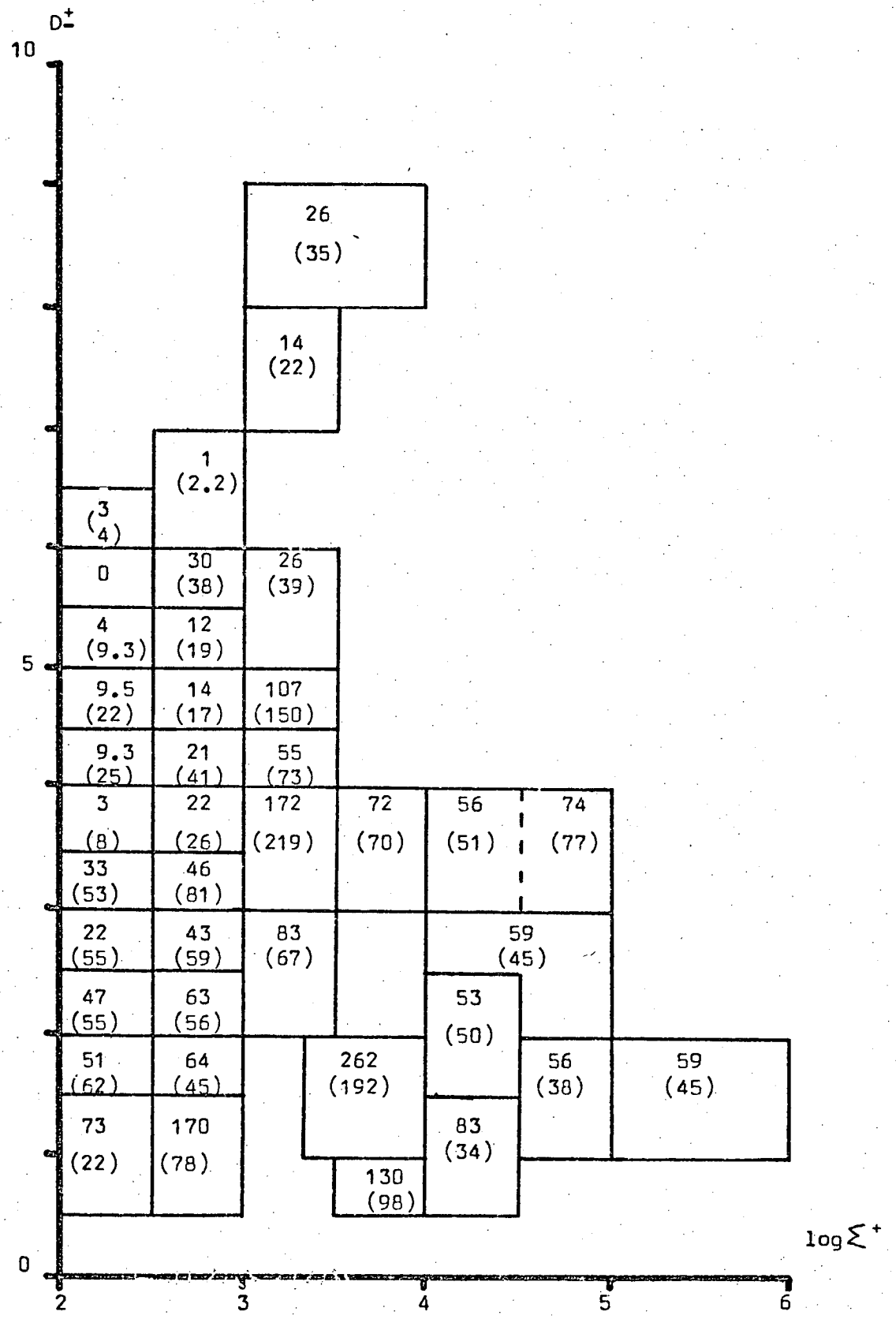
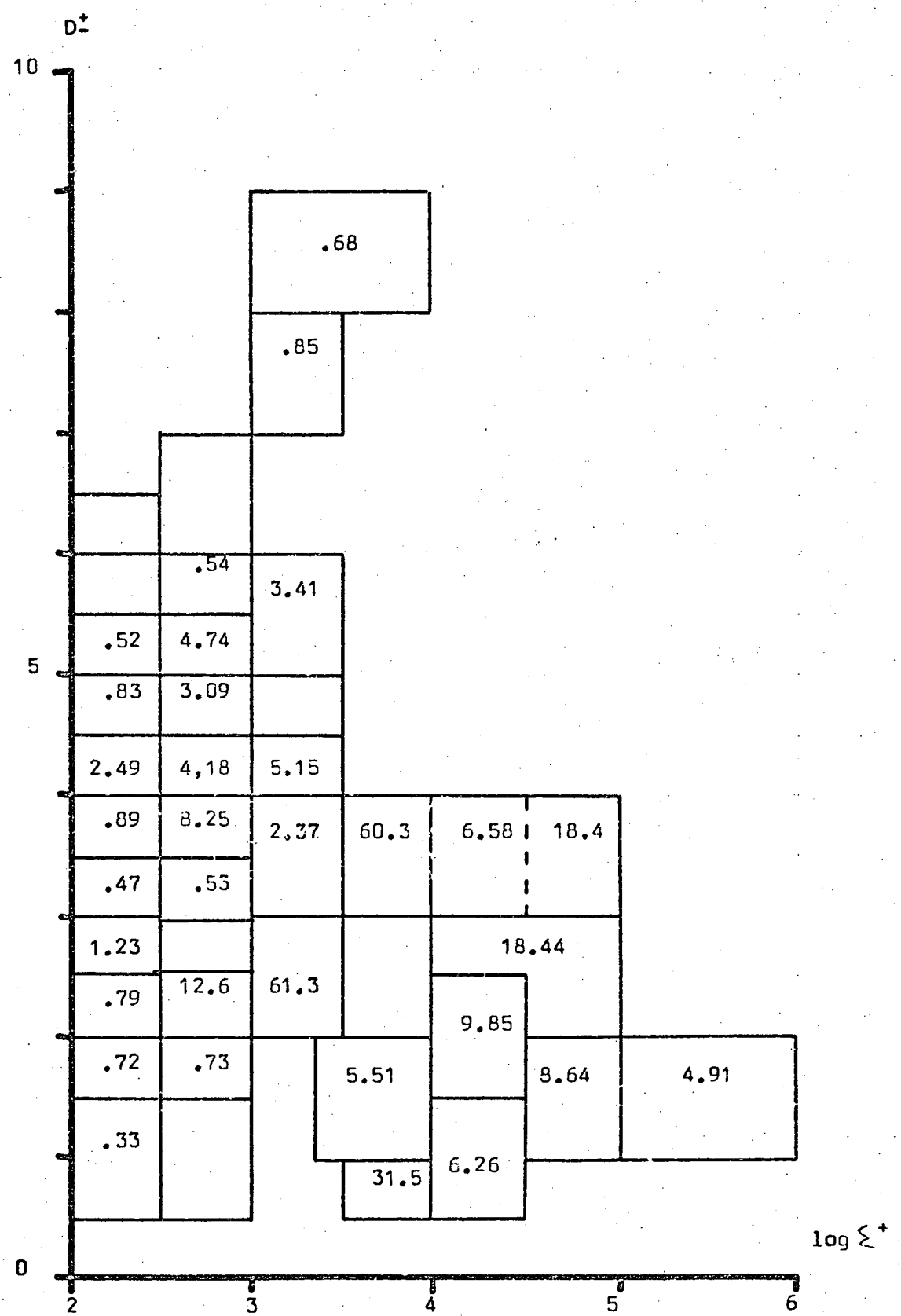


FIGURE 11.11 : TURBIDITY MEANS FOR WATERS GROUPED ACCORDING TO TOTAL CONCENTRATION AND STOICHIOMETRY.



It is possible to recognise that the highest values of turbidity occur in those waters near the edges of the distribution of $D^{\pm}$ and $\log\Sigma^{+}$. Further, in these waters, standard errors appear to be proportionately large. The most consistently low values of turbidity occur in the most dilute waters with a near-seawater stoichiometry. These observations are in accord with a geological origin for most of the suspended material. In the most saline waters suspended matter may consist of particles of salts of low solubility.

5. DISCUSSION

It is relevant to record here that the distance parameter employed above could have been constructed using more chemical characteristics than the seven relative ionic proportions chosen. It would have been possible to include , for example, pH in the calculation of weighted distance without disrupting the mathematical structure of the parameter. Had pH been included, the definition of the concentrations of silica, iron, etc. would probably have been better. The parameters used were those most easily to the Gibbs scheme of factors controlling water chemistry.

The notation used above has been constructed using the observed range of ionic proportions found for Tasmanian waters; in this respect, its use might not be valid for other areas. It has, however, facilitated the identification of some features which might occur widely.

The attainment of a maximum pH at $\log\Sigma^{+} \approx 5.2$ for the waters of near-seawater stoichiometry may be a general phenomenon: some highly saline waters in South Australia and Western Australia (Williams and Buckney, unpublished data) seem to continue the trend for pH to be low at high salinities.

One "type" of water is better defined than most others. At $D^{\pm} \approx 10$, the mean values of pH and silica concentrations are well-defined; iron concentrations and colour intensities are invariably low. These features are in accord with an

hypothesis of the sort advanced by Rodhe(1949) who proposed the existence of an equilibrium state among Swedish fresh waters; this equilibrium composition was shown to be about the same as the world average freshwater (WAFW) composition defined by Livingstone (1963). Gorham (1955, 1961) has criticised this hypothesis - particularly the implication that the WAFW is an end condition for an evolving freshwater. In this study, the WAFW would have $D^{\pm} = 6.99$, which is somewhat less than the maximum found for Tasmania, but near the upper limit for waters draining igneous rocks, and within the area in Fig. 11.5 for which $(pH + pSiO_2)$ is least variable.

It might be expected that for a given water with constant stoichiometry and total concentration, the variability of parameters such as pH, iron concentration, SiO_2 concentration, etc. would be inversely proportional to the precision with which these parameters are defined by the notation used. Similarly, since the range of $D^{\pm}$ is greatest for freshwaters, it would be expected that stoichiometry would be more variable in a given fresh water than in a saline water. It is likely, though, that the variability of these parameters would be at least partially influenced by factors such as catchment and water body morphometry, temperature, biotic influences, etc. , as described in Chapter 1

The notation used here has been applied to a description of the chemical nature of a large number waters from widely different catchments (see Buckney and Tyler, 1973a for a description of these). It is likely that if a comparable number of samples from a single rock type were treated in the same way, the parameters which do not contribute to Σ^+ and $D^{\pm}$ would be defined more precisely by the notation. Again, the precision with which the secondary chemical characters are defined depends upon the sizes (in terms of Σ^+ and $D^{\pm}$) of the groups of waters considered. The information here is not considered adequate for an investigation of the effect that a change of scale would have in this regard.

6. CONCLUSIONS

(i) The major ion chemistry of an inland water can be described in terms of its concentration and stoichiometry.

(ii) Stoichiometry of a water may be represented by the ratios $\frac{K18}{\Sigma^+}$, $\frac{S}{\Sigma^+}$ and by the distance between an origin and the point occupied by the water in the seven-dimensional space defined by the relative proportions of the major ions.

(iii) The binary notation: ($\log\Sigma^+$, $D^{\pm}$) is effective in defining the pH of waters to within narrow limits, indicating the possible existence of a major ion control of pH especially in the more acid waters.

(iv) The binary notation: ($\log\Sigma^+$, $D^{\pm}$) is less effective in defining silica and iron concentrations, colour intensity and turbidity.

(v) The ranges of pH and ($pH + pSiO_2$) are markedly restricted at high values of $D^{\pm}$, indicating the probable existence of an equilibrium state among geochemically-influenced dilute waters.

(vi) There is a maximum pH value attained at a $\log\Sigma^+$ value of about 5.2 ($S \approx 11‰$) among waters with a near-seawater stoichiometry, this being near the concentration value proposed (Buckney and Tyler, Unpublished) as the upper limit to the "fresh" waters.

(vii) It is concluded that most suspended material in Tasmanian waters is geologically-derived.

(viii) The conclusions drawn concerning the main features of and trends in the chemistry of Tasmanian waters (Buckney and Tyler, 1973a) are confirmed.

CHAPTER 111

FEATURES OF THE CHEMICAL VARIABILITY OF TASMANIAN INLAND WATERS

CONTENTS

ABSTRACT

Some problems of assessing chemical variability in inland waters are discussed. The variability of total concentration (represented as Σ^+) and of stoichiometry ($D^{\pm}$) are statistically related to climatic, morphologic and geological factors affecting the waters studied; the extent to which these influences can be assumed to control variability is assessed. Some chemical features of a few Tasmanian waters are reviewed.

1. INTRODUCTION

(A) Scope of this Treatment

Most Tasmanian waters are quite dilute (Buckney and Tyler, 1973a), though the range of concentrations is wide (T.D.S. from 0.01 to more than 120 g. l^{-1}). The seasonal behaviour of some freshwater lakes has been published (Buckney and Tyler, 1973b; Cheng and Tyler, 1973a; Croome and Tyler, 1972; Tyler and Buckney, 1974), though the identification of seasonal patterns has not been attempted. Other waters have been sampled either regularly or casually during the period 1970-74 and data from these (See Table 111.1) include figures for two of the most saline waters in Tasmania and cover about 60% of the observed stoichiometric range for Tasmania.

The literature describing major ion variability (Chapter 1) allows the identification of some possible controlling factors. These include:

(i) climatic variability

(ii) biology

(iii) morphometry of catchment and water body

(iv) geology

(v) flow rate

(vi) sediments

The relative importance of the first four of these has not been quantitatively guaged; this is attempted in this chapter. The influences of flow rate and of sediments are considered later.

(B) Assessment of Variability

Bayly (1966), Bayly and Williams (1966) and Timms (1970a) have used the observed range of parameters to represent variability, Timms also using the ratio maximum value/minimum value. Since even an intense sampling program might not include samples showing true maxima or minima of parameters, use will be made here of the standard deviation, S_x, of parameters.

2. RESULTS

The means, standard deviations (S_x) of Σ^+ and $D^{\pm}$ and sample sizes (n) for the waters used in this section are collected in Table 111.1. The locations of the waters are shown in Figure 111.1. The ternary diagrams (Figure 111.2) summarise the stoichiometric data, while morphometric parameters are presented in Table 111.2.

3. DISCUSSION

(A) Total Concentration

(i) Variability as a function of total concentration

The following equation describes the relation between standard deviation of Σ^+ (S_{Σ^+}) and mean Σ^+ ($\bar{\Sigma}^+$) for the waters sampled: (Figure 111.3)

$$\log S_{\Sigma^+} = 1.113 \log \bar{\Sigma}^+ - 1.111; r=0.982, n=26 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

i.e. $$S_{\Sigma^+} = \bar{\Sigma}^{+\,1.113} \times 0.0774$$

Thus, the variance of Σ^+ is greater than the mean value; that is, the frequency distribution of Σ^+ in a lake is overdispersed. A theoretical minimum value of Σ^+ ($= \bar{\Sigma}^+ - 2S_{\Sigma^+}$, for example) would be negative for some of the more concentrated waters sampled, indicating that (i) low values of Σ^+ are less frequent than would be expected of a normal frequency distribution of Σ^+, and (ii) high values of Σ^+ are more frequent than would be expected of a normal distribution. Thus, it is possible that for each water sampled there is an actual minimum total concentration; this may be the minimum total concentration of rainwater.

Equation (1) quantitatively confirms the observation of Bayly and Williams (1966) that the greatest absolute and relative fluctuations of total concentration occur in more saline waters.

The existence of such a definitive regression suggests that the main factors which determine the value of Σ^+ also determine the standard deviation of Σ^+. Thus,

TABLE III.1

MEANS, STANDARD DEVIATIONS AND SAMPLE SIZES OF Σ^+ AND $D^{\pm}$ FOR SOME TASMANIAN WATERS.

WATER	n	Σ^+ (/u eq/l)		$D^{\pm}$	
		MEAN	S	MEAN	S
L. Dulverton	6	21354	4192	2.586	0.204
Township Lagoon	7	776908	423077	1.700	0.188
L. Sorell	26	493	32.45	4.494	0.317
L. Crescent	26	546	77.81	4.230	0.228
L. Augusta	4	183	45.59	2.252	0.108
Great L.	5	233	32.44	4.625	0.470
Woods L.	17	471	33.62	4.140	0.383
Lagoon of Islands	18	1875	305.5	5.854	0.129
L. Dobson	31	325	37.95	5.101	0.358
Eagle Tarn	6	365	94.83	4.972	0.306
Beatties Tarn	4	226	18.84	3.211	0.252
Brownwater Lagoon	8	996	781.9	4.542	0.853
Dove Lake	4	149	40.63	2.888	1.492
L. Edgar	4	492	33.40	2.233	0.209
L. Pedder	9	362	114.6	2.038	0.408
Granton Lagoon	25	40120	5115.8	4.603	0.055
L. Leake	14	337	47.76	4.294	0.249
Tooms L.	13	383	40.23	4.286	0.942
L. Rowallan	7	235	24.21	4.934	0.703
L. Barrington	9	290	58.62	4.544	0.669
Grimes Lagoon	4	10583	65.99	4.023	1.127
Folly Lagoon	3	205910	50221	1.670	0.430
Calverts Lagoon	4	217938	146053		
Blackman's Lagoon	3	24917	2494	1.930	0.808
Derwent R.	19	655	90.92	2.813	0.055

TABLE 111.2

MORPHOMETRIC DATA FOR SOME TASMANIAN WATERS.

* Estimate based on assumed mean depth for shallow lakes.

WATER	Catchment Area (ha)	Lake Surface Area (ha)	Lake Volume (km^3)
L. Dulverton	4036	915	1.83×10^{-2} *
Township Lagoon	76.45	0.06	2.4×10^{-7} *
L. Sorell	9580	4713	1.15×10^{-1}
L. Crescent	15280	2365	3.5×10^{-2}
L. Augusta	22800	2072	4.14×10^{-2} *
Great L.	39600	15000	1.44
Woods L.	9320	1269	2.54×10^{-2} *
Lagoon of Islands	3365	939	
L. Dobson	101.9	8.25	1.64×10^{-4}
Eagle Tarn	32.14	0.82	2.73×10^{-6} *
Beatties Tarn	32.12	1.41	1.41×10^{-5} *
Brownwater Lagoon	84	10	1.0×10^{-5} *
Dove L.	508	82.56	1.72×10^{-2}
L. Edgar	650	38	7.6×10^{-4} *
L. Pedder	12424	970	1.46×10^{-2}
Granton Lagoon	1887	40	2×10^{-4} *
L. Leake	4900	550	1.5×10^{-2}
Tooms L.	6000	660	2.4×10^{-2}
L. Rowallan	34300	881	1.3×10^{-1}
L. Barrington	70600	780	2.3×10^{-1}
Grimes Lagoon	370	170	1.7×10^{-3} *
Folly Lagoon	83.3	18.25	7.3×10^{-5}
Blackman's Lagoon	198	18	1.8×10^{-4}

FIGURE 111.1 : SAMPLE SITES USED FOR THE STUDY OF CHEMICAL VARIABILITY IN TASMANIAN WATERS.

1. L. Dulverton
2. Township Lagoon
3. L. Sorell
4. L. Crescent
5. L. Augusta
6. Great L.
7. Woods L.
8. Lagoon of Islands
9. L. Dobson
10. Eagle Tarn
11. Beatties Tarn
12. Brownwater Lagoon
13. Dove L.
14. L. Edgar
15. L. Pedder
16. Granton Lagoon
17. L. Leake
18. Tooms L.
19. L. Rowallan
20. L. Barrington
21. Grimes Lagoon
22. Folly Lagoon
23. Calverts Lagoon
24. Blackmans Lagoon
25. Derwent River, Plenty.

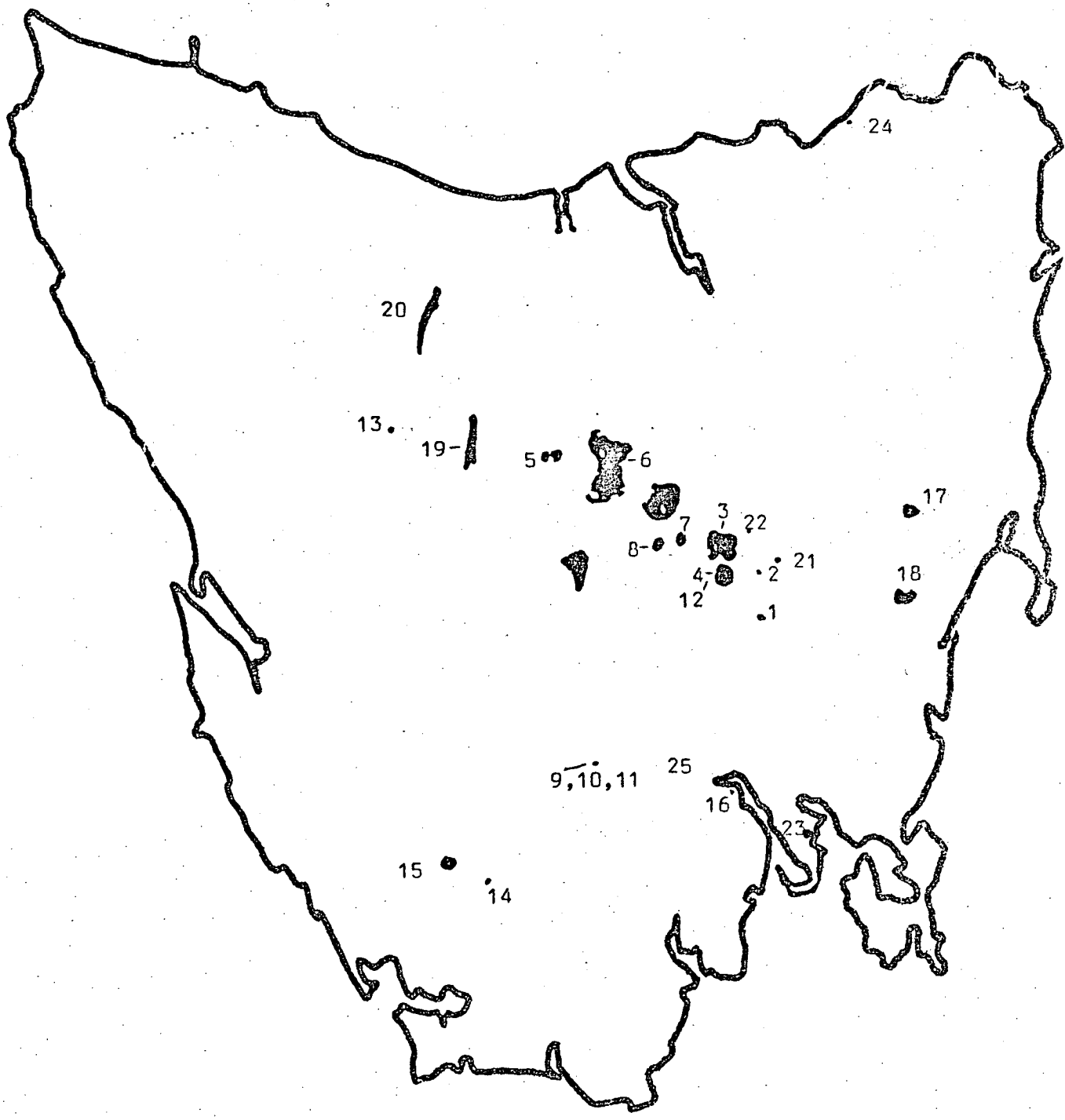

24
20
13
19
5
6
17
3
22
7
8
21
4
2
18
12
1
9,10,11
25
16
23
15
14

FIGURE 111.2 : DISTRIBUTIONS OF RELATIVE IONIC PROPORTIONS IN THE WATERS SAMPLED.

(2 PAGES)

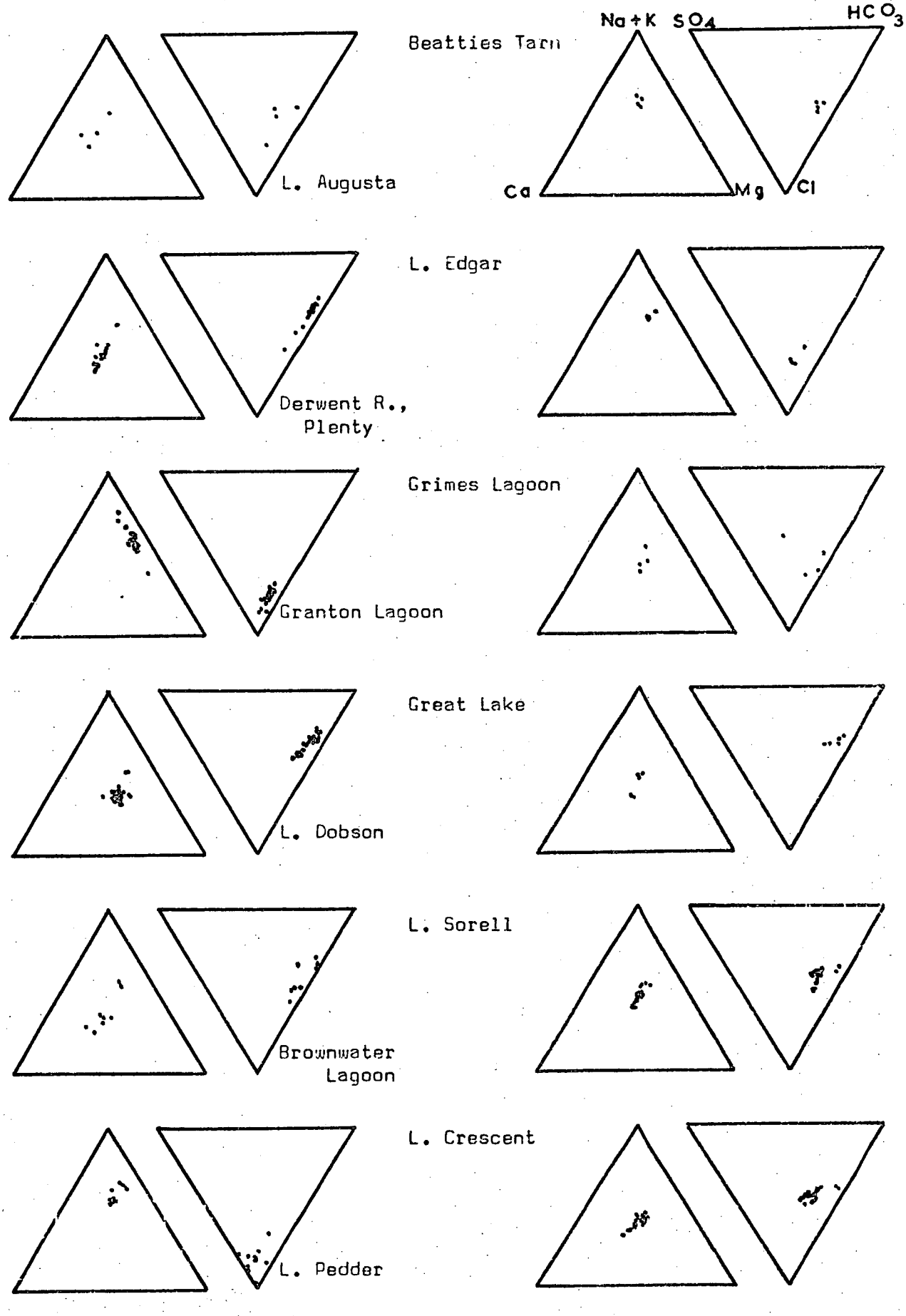

Beatties Tarn
Na+K
SO4
HCO3
Ca
Mg
Cl
L. Augusta
L. Edgar
Derwent R.,
Plenty
Grimes Lagoon
Granton Lagoon
Great Lake
L. Dobson
L. Sorell
Brownwater
Lagoon
L. Crescent
L. Pedder

FIGURE 111.2 (continued)

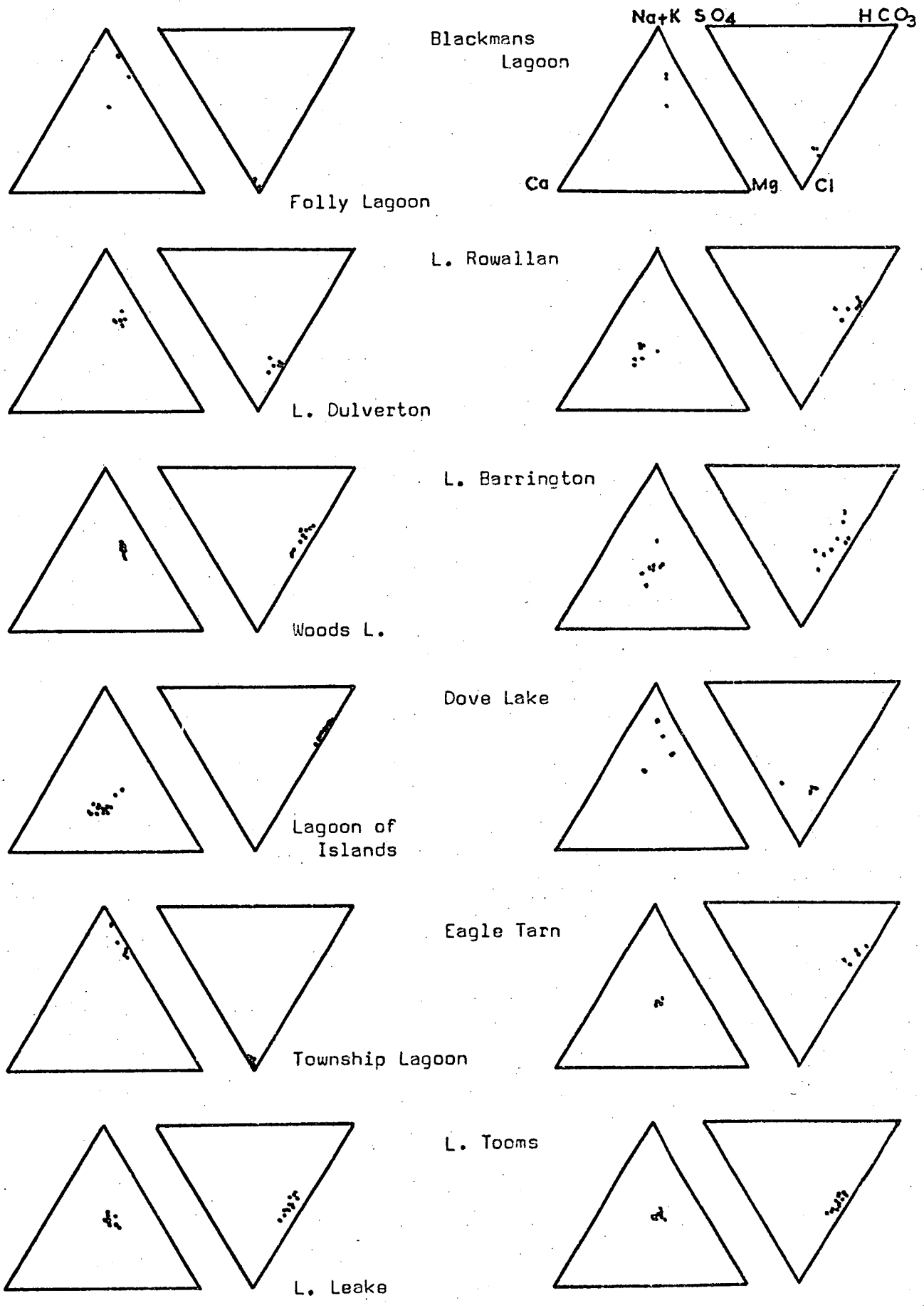
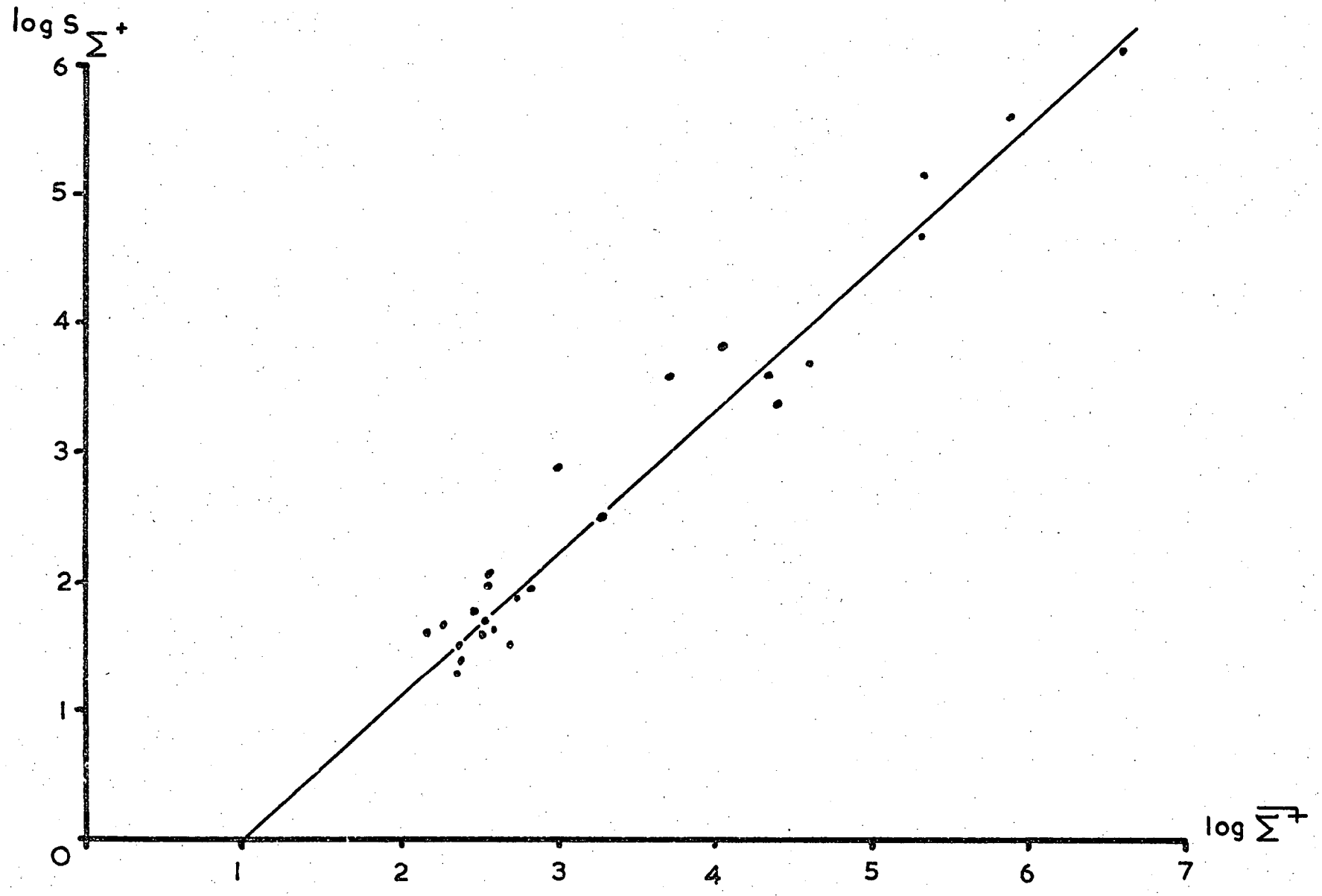


FIGURE 111.3 : CORRELATION BETWEEN STANDARD DEVIATION OF $\Sigma^+(S_{\Sigma^+})$ AND MEAN Σ^+ $(\overline{\Sigma^+})$.


log S Σ+
6
5
4
3
2
1
0
1
2
3
4
5
6
7
log Σ+

the value of the ratio $\frac{S_{\Sigma^+}}{\bar{\Sigma}^+}$ can be used as a convenient index of variability of concentration for a water.

(ii) Effect of climate on variability

Variability of total concentration can be expected to be a function of the variability of inflows and water loss. In the absence of adequate hydrologic data for all sites, it has been necessary to make use of the available meteorological data from the nearest (or most central) station for each catchment.

Variability of rainfall could be represented in a number of ways. If there are R separate days on which rain falls, the mean dry period, D, is $\frac{365}{R}$ days, and the mean shower intensity, I, is $\frac{T}{R}$, where T is the mean annual rainfall. In the treatment below, the variability of rainfall is defined by the equation:

$$V_R = D \times I = \frac{365T}{R^2}.$$

This parameter , which incorporates a term proportional to the mean dry period, may be relevant to a consideration of pulse effects.

The index of variability of concentration is correlated with V_R (Figure 111.4): $\frac{S_{\Sigma^+}}{\bar{\Sigma}^+} = 0.017\ V_R - 0.038$; $r = 0.579$, $n = 25$ ($p < 0.01$).....(2).

This agrees with the hypothesis that variability of total concentration is largely determined by climatic variability.

Most waters are more or less variable than equation (2) indicates. The deviations from this equation can be expected to be related to the morphometry of the lake basin and its catchment.

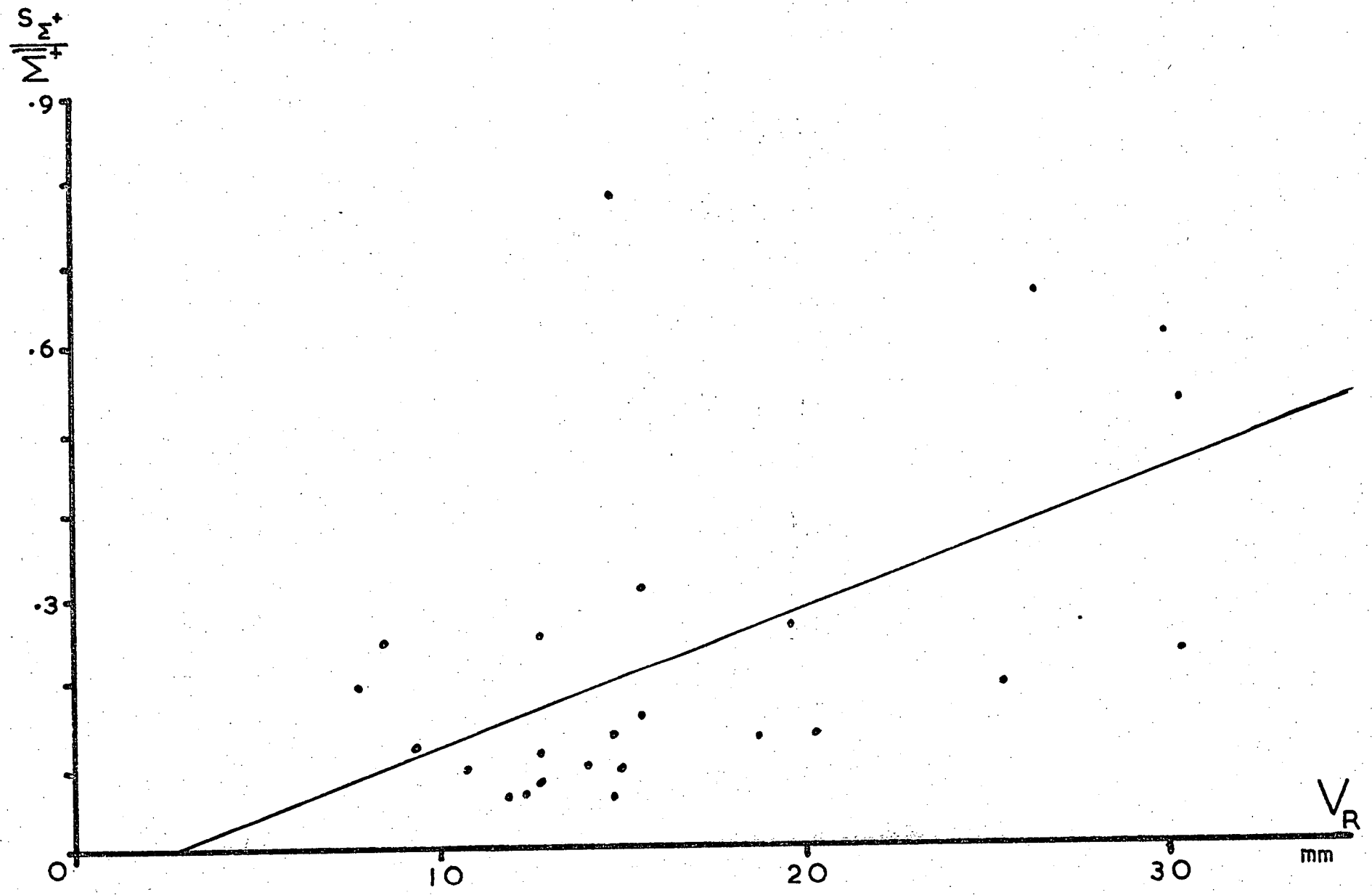
(iii) Effect of morphometry

None of the morphometric parameters are significantly correlated with the coefficient of variability of concentration, $\frac{S_{\Sigma^+}}{\bar{\Sigma}^+}$.

The relative importance of climatic variability and the morphometric parameters can be guaged by repeatedly calculating regressions - initially between the ratio $\frac{S_{\Sigma^+}}{\bar{\Sigma}^+}$ and V_R,- and then between the deviations from this regression and each of the morphometric parameters.

Several hypotheses can be formulated to predict the effect that

FIGURE 111.4 : THE VARIATION OF THE COEFFICIENT OF VARIABILITY OF TOTAL CONCENTRATION, $\frac{S_{\Sigma^+}}{\overline{\Sigma^+}}$, WITH CLIMATIC VARIABILITY (V_R).


S_{Σ^+}
Σ^+
.9
.6
.3
0
10
20
30
V_R
mm

morphometric parameters have on variability of concentration. The two simplest hypothesis are:

(a) Morphometric variables reduce the climatically-induced variability;

i.e. $\frac{S_{\leq}^{+}}{\Sigma^{+}} = k_1 \sqrt{R} - F$, where k_1 is constant and F is some function related to morphometry.

(b) Morphometry may have a synergistic effect on the climatically-induced variability; the simplest equation describing such a situation would be:

$\frac{S_{\leq}^{+}}{\Sigma^{+}} = k_2 \sqrt{R} \times M$, where k_2 is constant and M is a morphometric factor.

Both hypotheses yield similar results as to the relative importance of $\sqrt{R}$ and the morphometric variables, but hypothesis (b) is statistically more definitive. The following equation best accounts for the variation of $\frac{S_{\leq}^{+}}{\Sigma^{+}}$:

$$\log \frac{S_{\leq}^{+}}{\Sigma^{+}} = 0.52 \log \sqrt{R} - 0.01 \log V - 0.07 \log \bar{z} + 0.05 \log \frac{CA}{SA} - 1.41 \quad \ldots(3$$

$$(r = 0.63,\ n = 23,\ p\ \ 0.01)$$

where V is lake volume (km^3) CA and SA are catchment area and surface area respectively (in ha) and $\bar{z}$ is mean depth (m). The plot is shown in Figure 111.5.

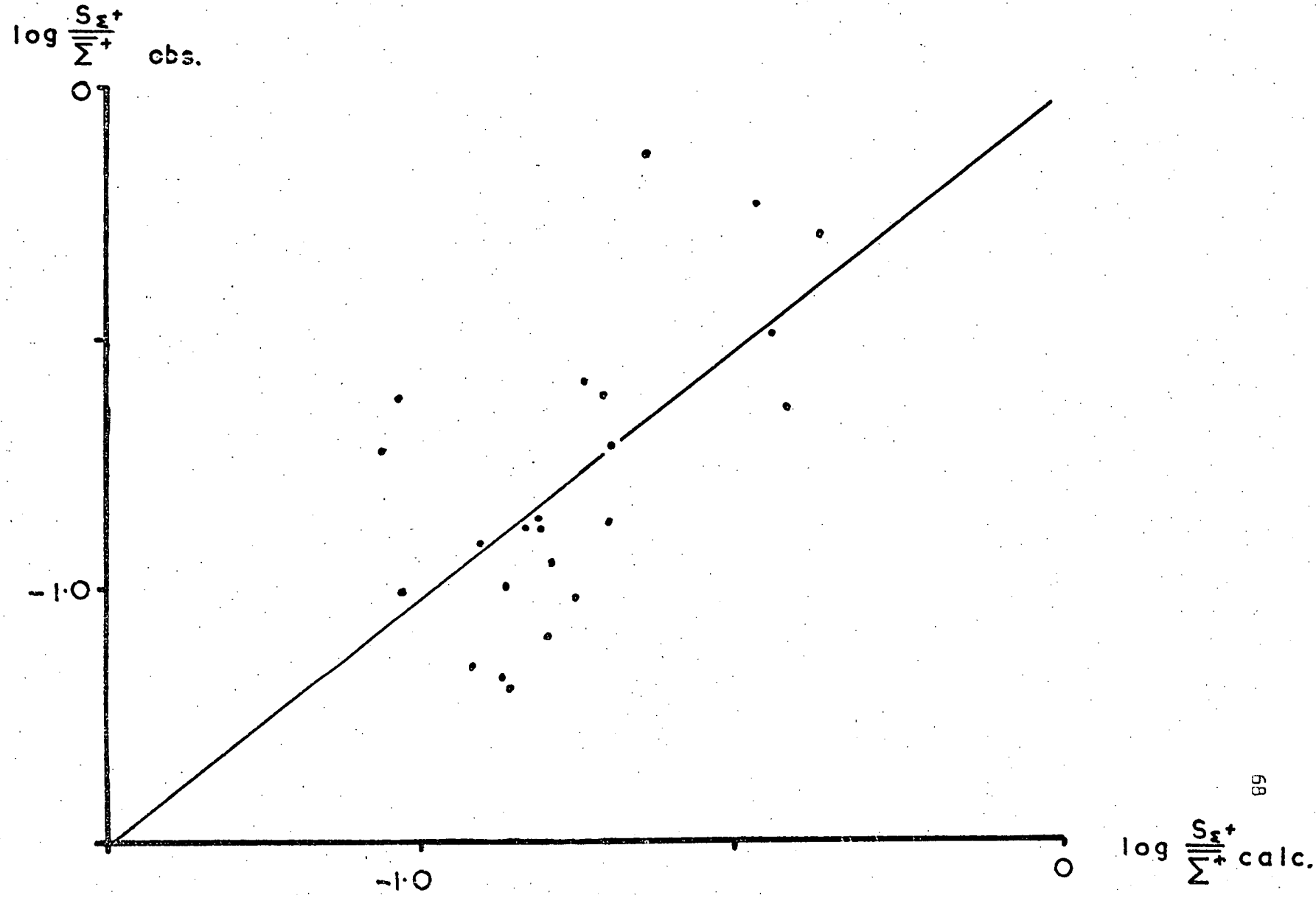
Equation (3) indicates that a 10 fold increase in $\sqrt{R}$ would approximately treble $\frac{S_{\leq}^{+}}{\Sigma^{+}}$, while similar increases in the other parameters would barely change $\frac{S_{\leq}^{+}}{\Sigma^{+}}$.

During the construction of equation (3) some features were obvious. These were:

(a) The ratio $\frac{CA}{SA}$ was statistically more relevant to the problem than CA and SA separately. This partially supports the assertion of Timms (1970a) who claimed that the renewal ratio, $\frac{CA}{SA}$ (Ravera and Tonolli, 1956) exerted a marked influence on variability of total concentration (The regression obtained by Timms contained only four points unevenly spaced and was probably invalid).

(b) The introduction of the renewal ratio term effectively introduced a further volume term with $\bar{z}$ already present ($V = \bar{z} \cdot SA$). Hence, while volume

FIGURE 111.5 : CORRELATION BETWEEN THE OBSERVED AND CALCULATED (equation 3, in text) VALUES OF THE COEFFICIENT OF VARIABILITY OF TOTAL CONCENTRATION.


log $\frac{S_{\Sigma^+}}{\Sigma^+}$ obs.
0
-1·0
-1·0
0
log $\frac{S_{\Sigma^+}}{\Sigma^+}$ calc.

per se influences variability of total concentration, shape is probably at least as important.

(c) At no time was there any indication that the saline waters ought to be considered separately. However, since mean concentration appears on the left of the equation, total concentration can be expected to exert a control on variability (as shown in equation (1)).

Other factors undoubtedly influence variability. These have been discussed by Gorham (1961) and include petrology, topography and vegetational influences. Small or shallow waters might experience a buffering influence exerted by exchanging or decomposing sediments. The term V_R was intuitively derived and relates to long-term rainfall data for the sites considered; samples were collected between 1970 and 1974. Thus, equation (3) ought not be viewed as anything more than an assessment of the relative importance of the variables considered.

Climatic variability is by far the most important control on variability of total concentration. Total volume is probably least important. Mean depth and renewal ratio exert an intermediate effect.

(B) The Concentrations of the Ions

The standard deviation of the concentration of each of the major ions bears a similar relation to the mean concentration as was observed for total concentration. The equations are:

$$\log S_{Na} = 1.232 \log (\bar{Na}) - 1.288; \quad r = 0.964$$

$$\log S_{K} = 1.085 \log (\bar{K}) - 0.508; \quad r = 0.975$$

$$\log S_{Ca} = 1.229 \log (\bar{Ca}) - 1.211; \quad r = 0.980$$

$$\log S_{Mg} = 1.192 \log (\bar{Mg}) - 1.197; \quad r = 0.968$$

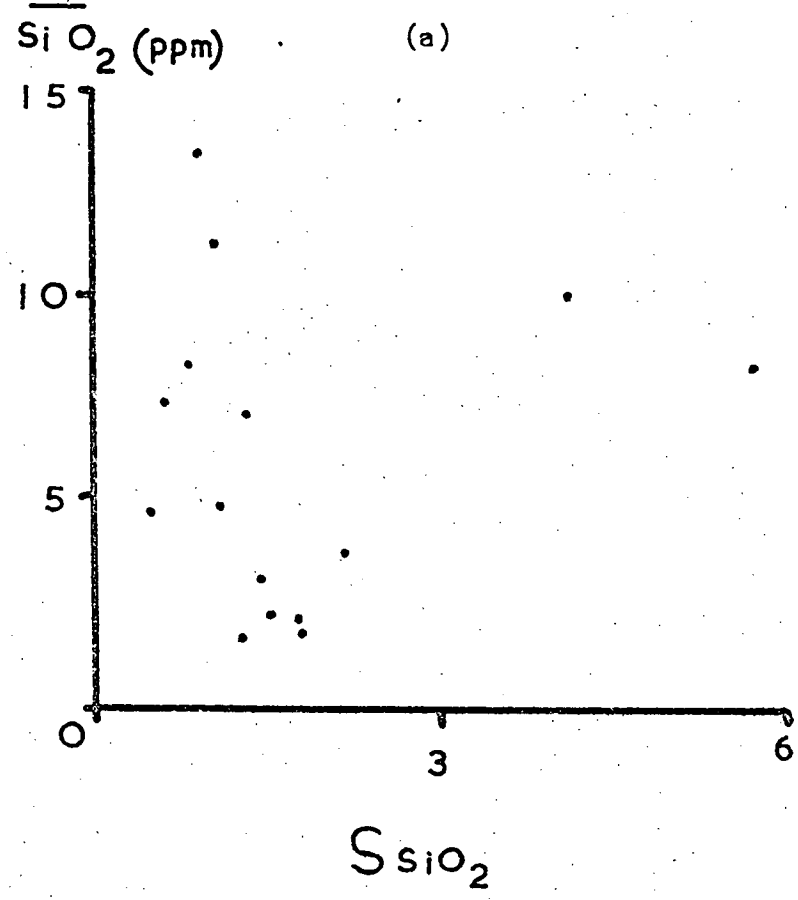
$$\log S_{Cl} = 1.145 \log (\bar{Cl}) - 1.048; \quad r = 0.971$$

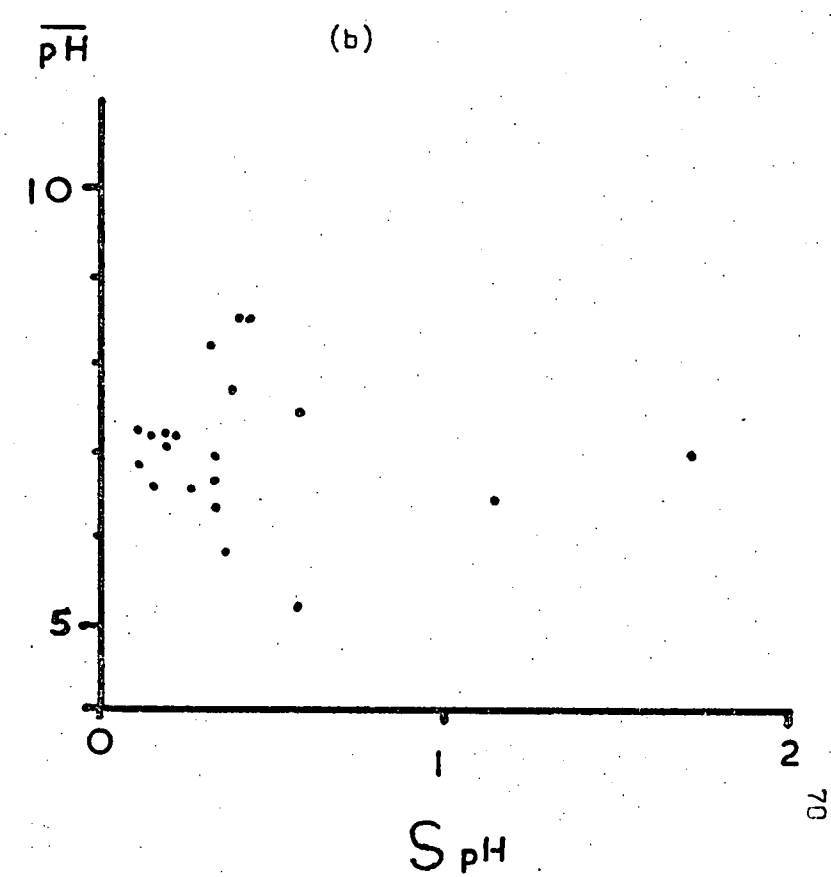
$$\log S_{SO_4} = 1.176 \log (\bar{SO_4}) - 0.776; \quad r = 0.981$$

$$\log S_{Alk} = 1.103 \log (\bar{Alk}) - 0.926; \quad r = 0.892$$

The major ions can be expected to display a variability which is relatively

FIGURE 111.6 : PLOTS OF STANDARD DEVIATIONS AGAINST MEANS FOR (a) SiO_2 AND (b) pH FOR THE WATERS SAMPLED.


$\overline{SiO_2}$ (ppm)
(a)
15
10
5
0
3
6
S_{SiO_2}


$\overline{pH}$
(b)
10
5
0
1
2
S_{pH}

greater at high concentrations than at low concentrations.

The plots of S_{SiO_2} against mean concentration of SiO_2 and of S_{pH} against $\bar{pH}$ are shown in Figure 111.6. Apart from Lagoon of Islands and Granton Lagoon, which show extremely variable silicon concentrations, there is a vague trend for Si concentration to be less variable at high concentrations (about 13 ppm SiO_2). The smallest variability of pH occurs at about pH = 7.1; the water with the most variable pH is the Derwent River, the only lotic site included.

(C) Stoichiometry

The distributions of $S_{D^{\pm}}$ over the ranges of $\bar{D}^{\pm}$ and $\log \bar{\Sigma}^{+}$ for the lakes considered are shown in Figures 111.7 and 111.8 respectively. $S_{D^{\pm}}$ is highest at low total concentrations, as suggested in Chapter 11. Large stoichiometric variability is not, however, a defining characteristic of dilute waters.

In broard terms, the ions calcium, bicarbonate and to a smaller extent magnesium, sulphate and potassium have a geological origin while sodium and chloride (perhaps also magnesium and sulphate) are derived from the atmosphere (Gibbs, 1970; Gorham, 1961). Hence, the ratio of catchment area to lake surface area can be expected to control stoichiometry, since rain falling directly on the water surface will tend to produce a stoichiometry similar to seawater, while catchment runoff will result in enrichment of (mainly) alkaline earth bicarbonates. As indicated in Chapter 1, biological influences may act to obscure such effects. Other influences may be climate, and other morphometric parameters, as well as geology.

The available climatic and morphometric data allow the derivation of equation (4) below, for lakes draining dolerite catchments (see Buckney and Tyler, 1973a; for a summary of Tasmania's geology).

$$S_{D^{\pm}} = 0.25 \log \frac{CA}{SA} - 0.80 \log T + 0.32 \log \bar{D}^{\pm} + 1.53; \quad (r = 0.62, n = 14 \; p \; 0.07) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where T is the mean annual rainfall (in mm.).

During the derivation of equation (4), the terms $\bar{z}$, V and $\sqrt{R}$ were ineffective in improving the correlation. The appearance of the term T might reflect the fact

that reliability of rainfall in Tasmania is broadly proportional to the total rainfall (Langford, 1965); hence T may be relevant as a measure of rainfall variability. It would appear that those factors which determine the value of $D^{\pm}$ (i.e. geological influences) enhance the variability of stoichiometry.

The two most deviant points from equation (4) are Lake Augusta and Lagoon of Islands. In the former, the observed variability is greater than expected, perhaps because the lake fluctuates greatly in size. In the latter, a marked stabilisation of stoichiometry is evident (see section D, below); this might reflect the influence of the submerged reed mat and floating islands. (Tyler, unpublished).

Equation (4) has been used to calculate expected values of $S_D^{\pm}$ for waters other than those on dolerite. This results in the obliteration of the regression between observed and calculated values ($r = 0.036$). Thus, quite apart from the correction for $D^{\pm}$, there is a strong indication that a factor relating to geology per se is required to adequately account for stoichiometric variability. Perhaps the best statement of such an effect would be that stoichiometric variability depends on the weathering and water - transport characteristics of the catchment. The most variable waters relative to equation (4) are Dove Lake, Lake Pedder and Blackmans Lagoon; all have inert catchments (see Buckney and Tyler, 1973a and 1973b).

As is the case for total concentration, there has been no indication that the saline waters are different from the more dilute waters, though since T appears in equation (4), the waters in dry areas can be expected to be stoichiometrically less variable.

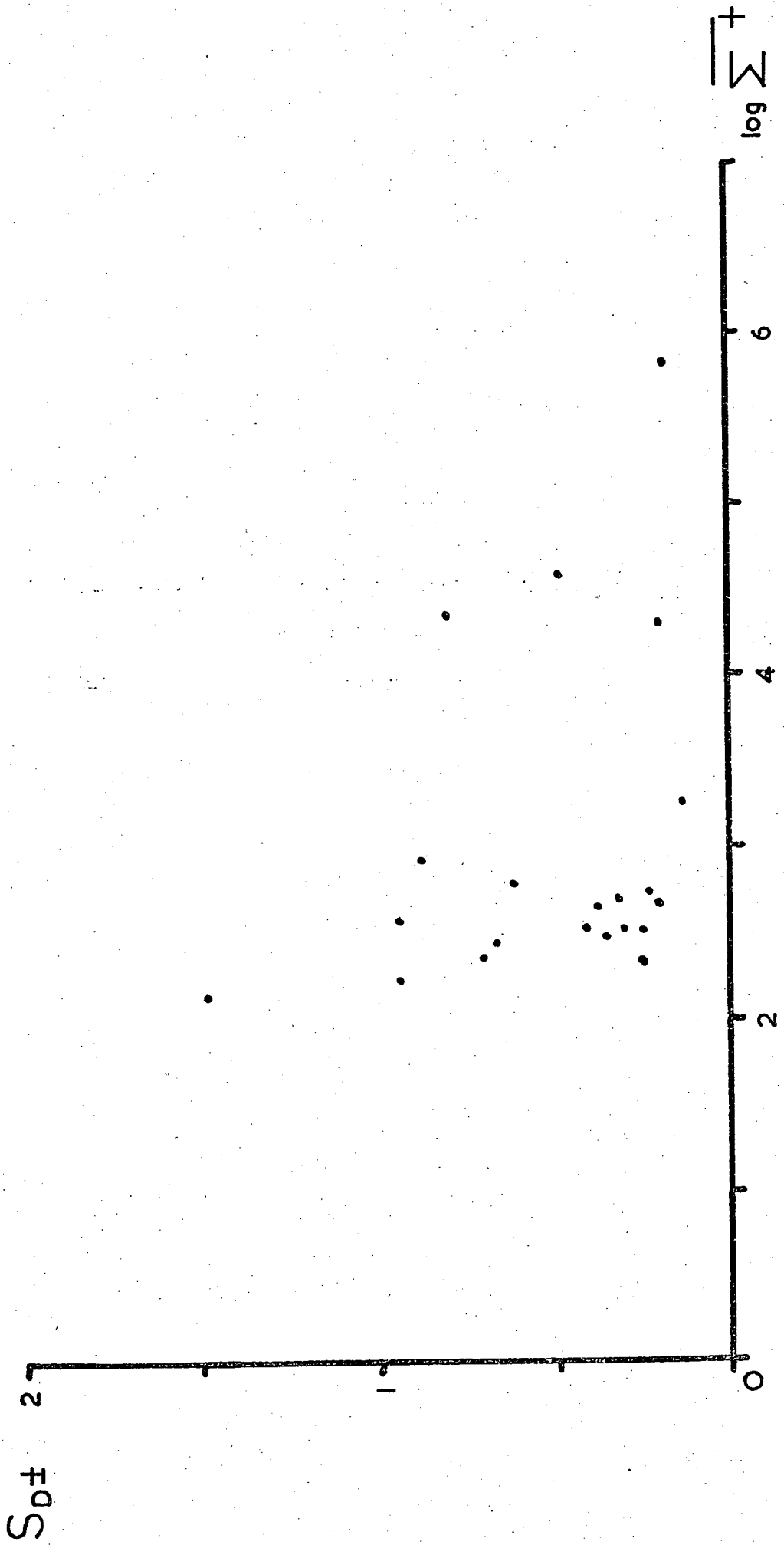
Factors which limit the wider applicability of equation (4) are largely the same as those for equation (3).

Since climate can be recognised as the most important feature controlling variability of total concentration and of stoichiometry, then in the simplest situation, change in total concentration can be viewed as an estimator of the

FIGURE 111.7 : DISTRIBUTION OF THE STANDARD DEVIATION OF $D^{\pm}$ OVER THE RANGE OF ITS MEAN.

S_{D^+}
2
1
0
1
2
3
4
5
6
D^+

FIGURE 111.8 : DISTRIBUTION OF THE STANDARD DEVIATION OF $D^{\pm}$ OVER THE RANGE OF THE MEAN TOTAL CONCENTRATION IN TASMANIAN WATERS.


log |M|+
0
2
4
6
-1
2
Sp+

influences acting to change stoichiometry. Below are collected some observations on a few waters for which sampling has been frequent.

(D) Some observations on Chemical Changes in Particular Waters

Lagoon of Islands (Figure 111.9a) displayed a marked fall in concentration during 1970; this accompanied an artificial rise in water level (Tyler, unpublished). The pre-impoundment concentration was restored during 1971 and 1972. During this period the stoichiometric stability was remarkable in view of the change in hydrology. The rise in water level almost certainly caused the deterioration of large quantities of the submerged and floating vegetation and would have resulted in the release of organically-bound solutes. The stoichiometric constancy therefore indicates that the chemistry of Lagoon of Islands has been stabilised by the uptake and release of material by the vegetation of the lake.

Brownwater Lagoon (Figure 111.9b) is semi-permanent and displayed a general rise of total concentration between 1969 and 1972; this suggests that a relatively arid period was prevailing during that period. Stoichiometric variability in the lagoon was great and this might reflect the substantial changes in surface area.

Lake Pedder (Figure 111.9c) illustrated a stoichiometric variability somewhat greater than Lagoon of Islands. A general rise in concentration was evident between 1969 and 1972. The pulse referred to in Chapter 1 (see also Buckney and Tyler, 1973b) is illustrated.

Lake Crescent (Figure 111.9d) showed a tendency for D^{+}_{-} to rise erratically after each of the floods (early 1969 and early 1970), while the nearby and contributing Lake Sorell (Figure 111.9e) is much less directional in its stoichiometric response to similar influences. Cheng and Tyler (1973a) emphasized the ability of Lake Crescent to "obstinately maintain its character" despite substantial changes in flow regimes, and inferred that the sediments and

FIGURE 111.9 : VARIATION OF LOG Σ^+ AND $D_{\pm}^{\pm}$ FOR SOME SELECTED TASMANIAN WATERS.

(2 PAGES)

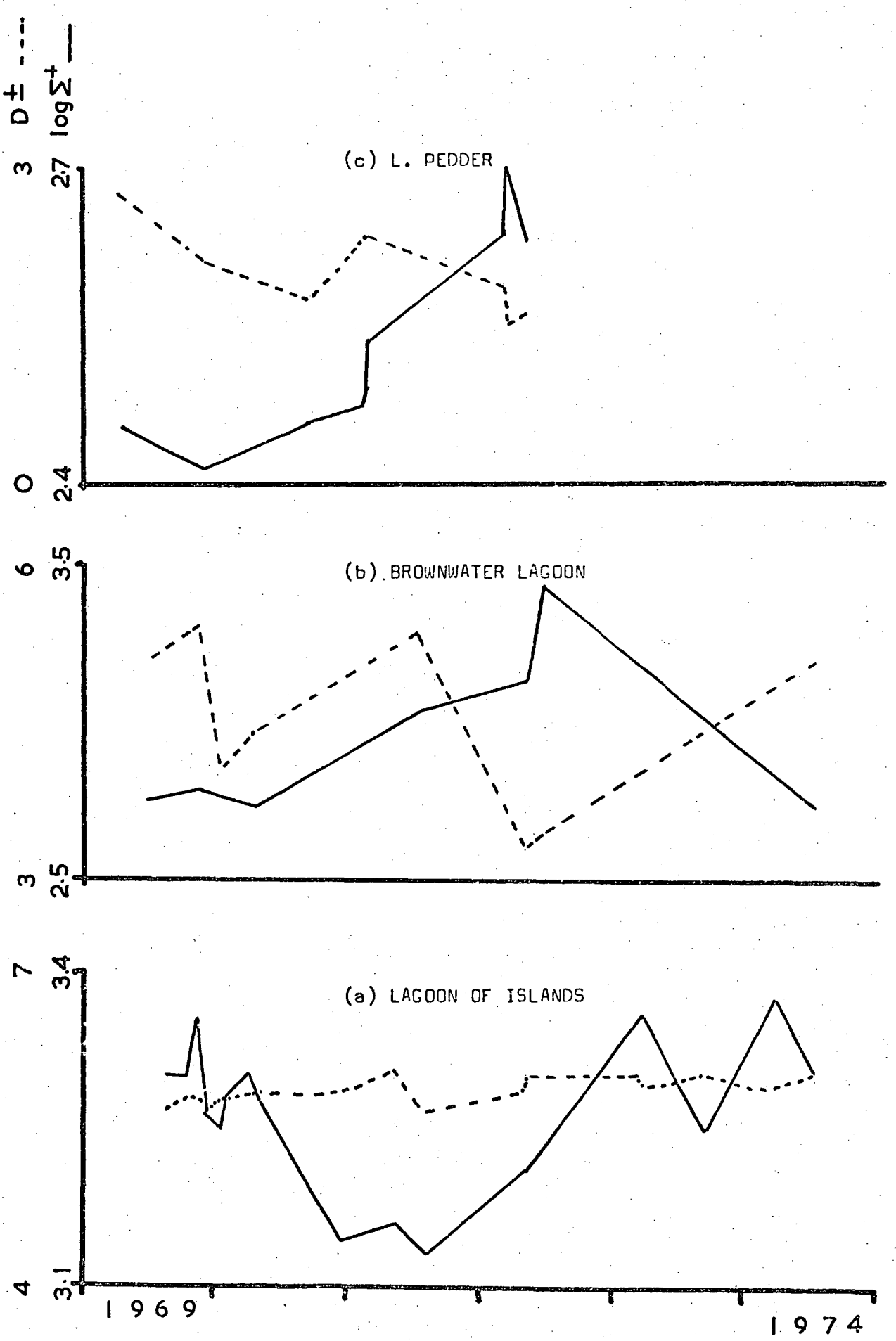
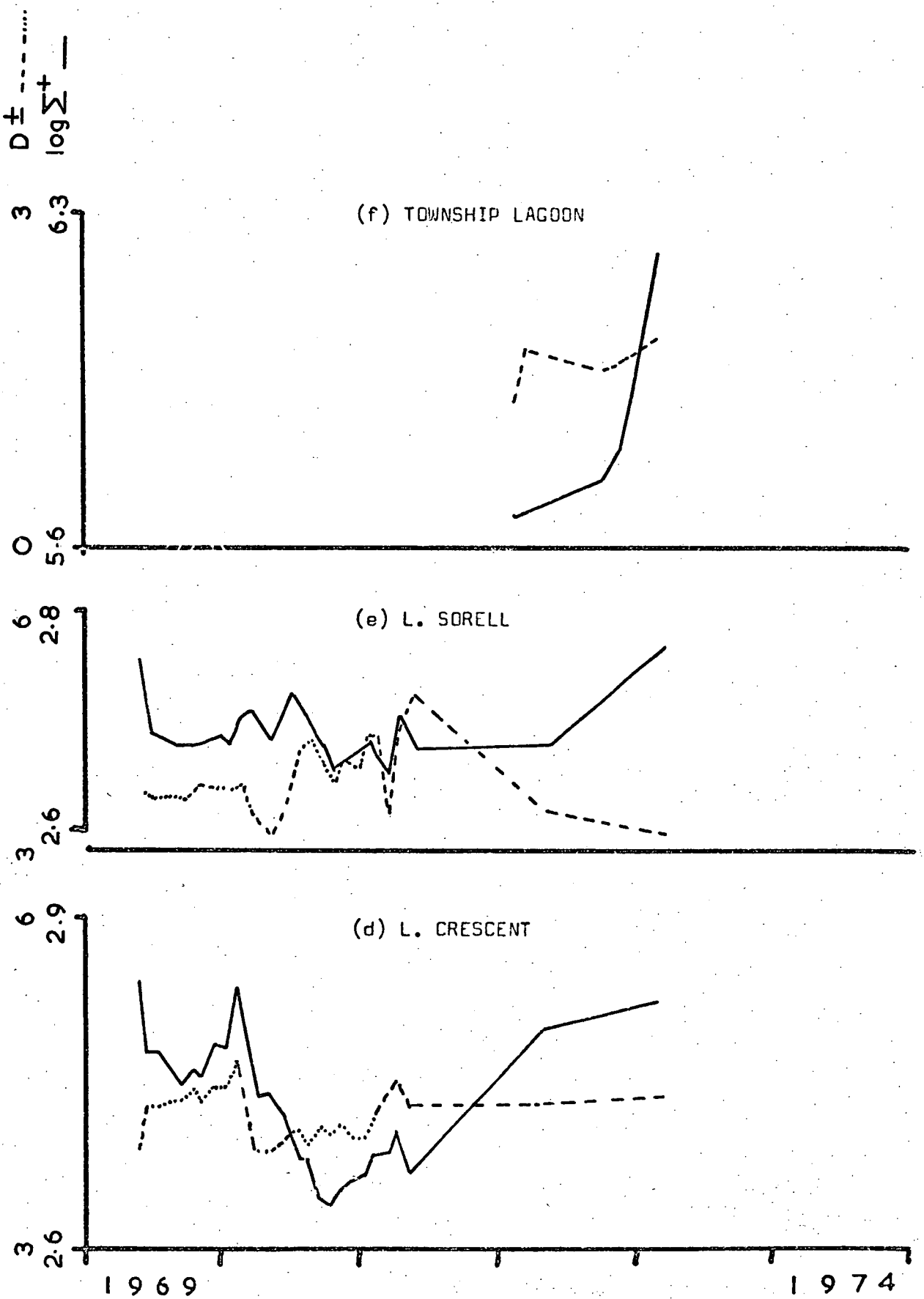

D± ----
log Σ+ ——
3
2.7
0
2.4
(c) L. PEDDER
6
3.5
3
2.5
(b) BROWNWATER LAGOON
7
3.4
4
3.1
(a) LAGOON OF ISLANDS
1969
1974

FIGURE 111,9 (continued)



marshes of Lake Crescent exerted an important influence on its chemistry; the data as presented here illustrate a behaviour in keeping with that hypothesis.

The saline Township Lagoon (Figure 111.9f) provides evidence that the relatively arid period identified above probably extended to 1973. The stoichiometric invariability was typical of saline waters.

Equations (3) and (4), above, provide an estimate of the relative importance of several factors determining chemical variability in waters. The observations on particular lakes indicate that biological factors and sediments (at least) may be important local factors affecting variability.

The theoretical "ideal" lake formulated in Chapter 1 is not approached by any of the waters considered here. Figure 111.9 provides some evidence that these waters generally have behaved like waters experiencing frequent pulses of varying intensity. There are a number of situations where marked increases of concentration have been followed by equally marked decreases of concentration and of $D_{\pm}^{+}$. Thus, flow regime effects seem to be important in determining hydrochemical features.

4. CONCLUSIONS

1. Among Tasmanian waters the standard deviations of total concentration, and concentrations of the major ions are proportional to a power of their means.

2. Climate is recognised to be by far the most important factor determining chemical variability of inland waters.

3. Morphometric parameters are probably of much less importance in determining chemical variability though total volume, lake shape and catchment morphometry are relevant to a consideration of variability.

4. Geological factors are important in influencing stoichiometric variability.

5. Sediments and biological effects may be very important locally in controlling stoichiometric phenomena.

6. Some of the most dilute waters show the greatest stoichiometric variability; there is no evidence that the factors controlling chemical variability are fundamentally different for saline waters.

CHAPTER 1V

CHEMICAL ASPECTS OF THE BEHAVIOUR OF THREE TASMANIAN WATERS

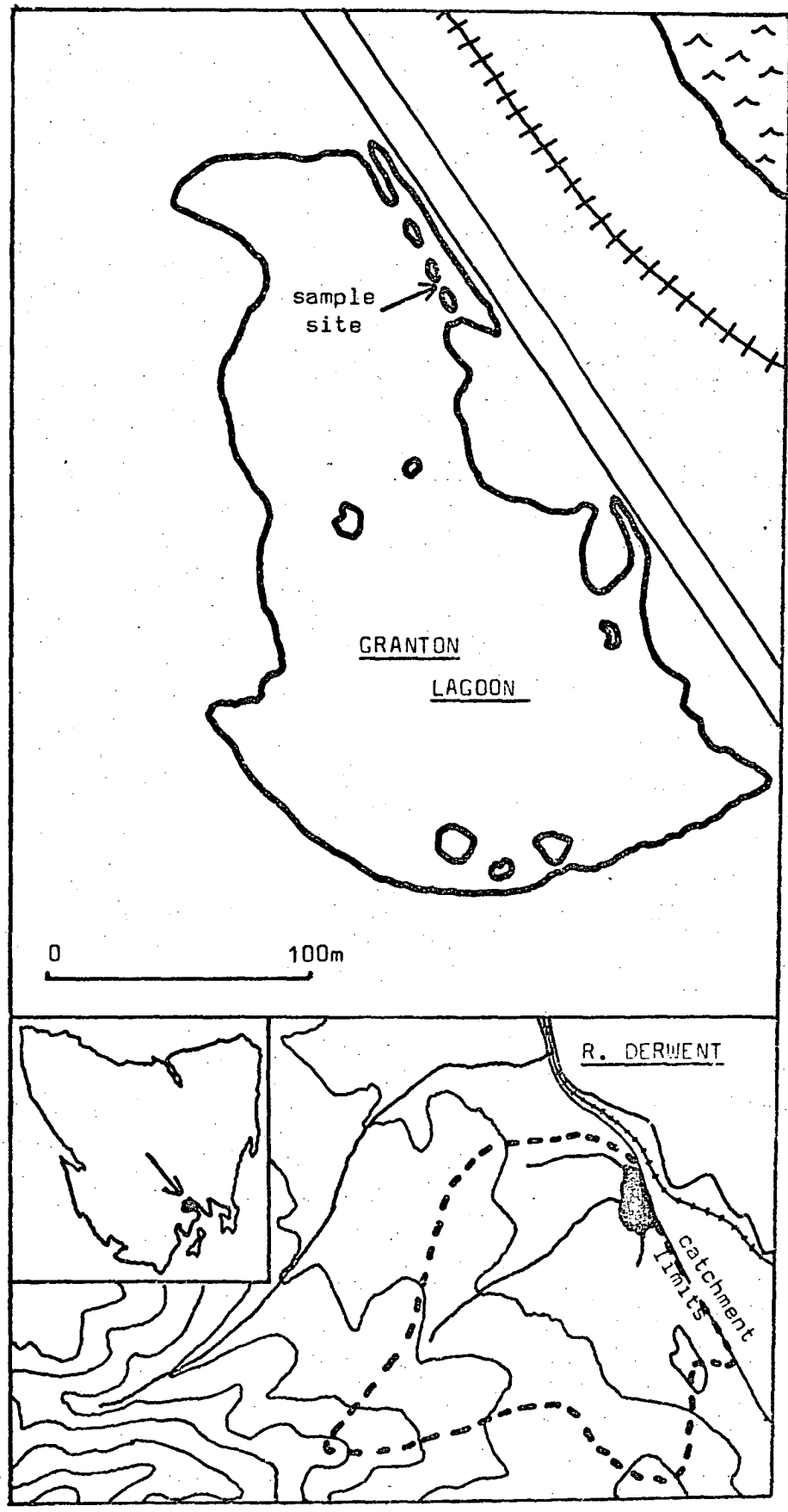
CONTENTS

ABSTRACT

The chemical behaviour of one lotic and two lentic waters are described. The interrelations between various chemical characters are investigated. In particular, the relations between total concentrations and stoichiometry are examined. The influence of physical factors - particularly flow rate - and of biological factors are explored.

FIGURE 1V,1 : GRANTON LAGOON - LOCATION AND MAIN FEATURES OF THE CATCHMENT.

Contour interval 50m.


sample
site
GRANTON
LAGOON
0
100m
R. DERWENT
catchment
limits

PART 1. THE CHEMISTRY OF GRANTON LAGOON

1. INTRODUCTION

Publications describing chemical changes in Tasmanian waters (Buckney and Tyler, 1973b; Cheng and Tyler, 1973a; Croome and Tyler, 1972) have dealt with fresh waters. The following describes the major features of a water which is considerably more concentrated than these, although it is not saline in the sense used by Buckney and Tyler (Unpublished *).

Granton Lagoon was formed when a marginal swamp of the Derwent River about 9km north of Hobart was isolated by the construction of a road (in 1818) and railway enbankment (near the end of last century). The Lagoon was declared a wildlife sanctuary in 1938. The catchment is mostly mudstone of Permian age (Spry and Banks, 1962) which supports a dry schlerophyll forest which has been partly cleared for farming.

Yasin (1967) conducted a brief study of the Lagoon, describing it as temporary. The basin was nearly dry in the summer of 1967, but filled soon after and has remained at least partially full since that time. Figure 1V.1 shows the location and main features of the catchment.

2. RESULTS

Morphometric data are summarised in Table 1V.1. Chemical data are presented in Table 1V.2 and summarised in Figure 1V.2. The stoichiometric features are included in Figure 111.2.

3. DISCUSSION

Total concentration (as Σ^+, Fig. 1V.2.a) showed erratic rises from about mid-year to the ends of the years. Discernible falls occurred after the summer periods (Dec. - Feb.), during or after the periods of heavy rainfall. During 1972-73 total concentration was about 60% of that recorded by Yasin for

* See appendix for summary

TABLE 1V.1

MORPHOMETIC DATA FOR GRANTON LAGOON

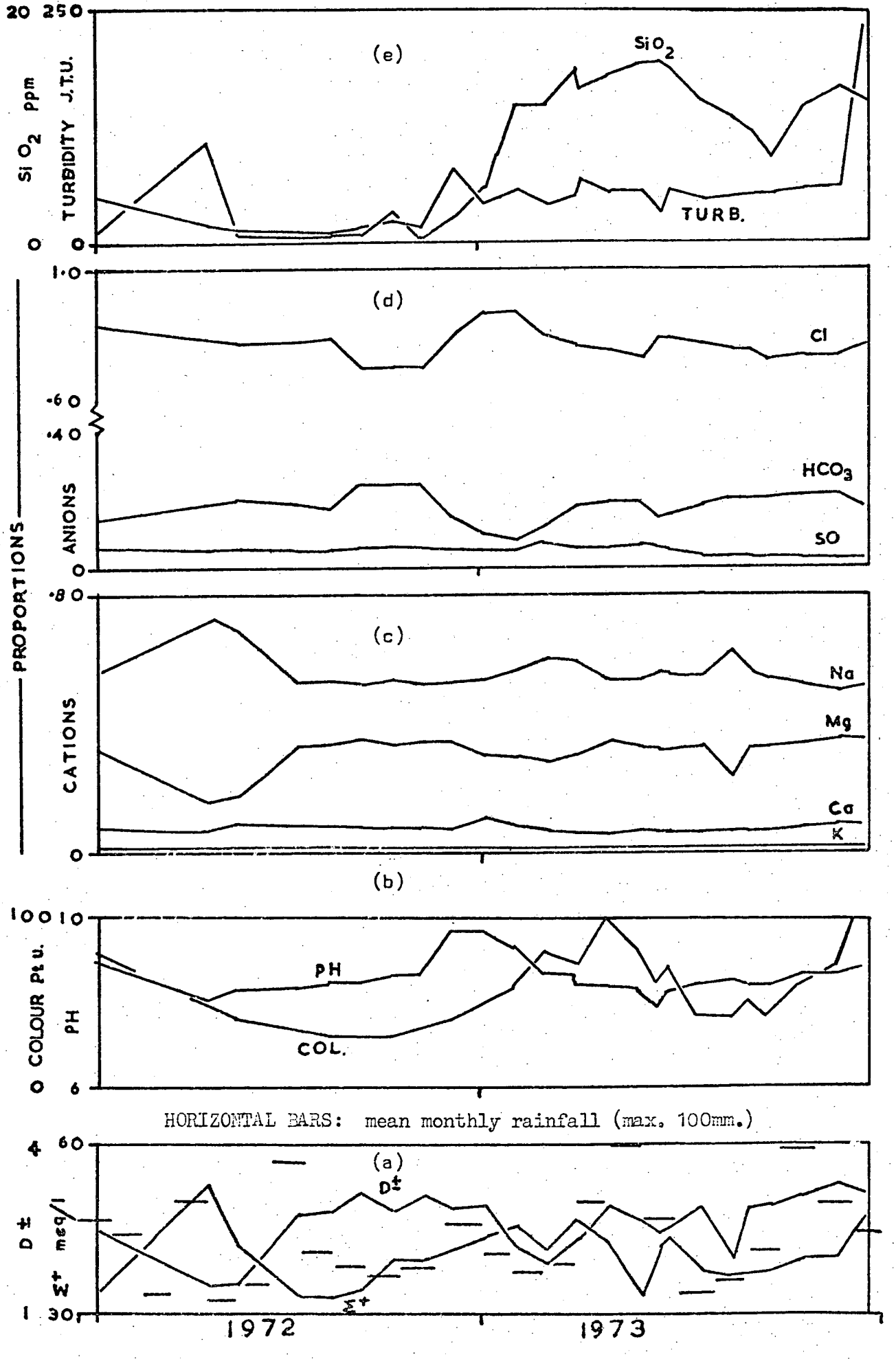
YEAR	1967 (Yasin 1967)	1972
Catchment Area (ha)		1887
Surface Area (ha)	4	40
Volume (m^3)		2×10^5
Perimeter (m)		960
Max. depth (m)	0.6	

TABLE 1V.2 THE MAJOR ION CHEMISTRY OF GRANTON LAGOON WATER

DATE	K18 m Scm^{-1}	Colour Pt Units	Turbidity J.T.U.	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3 +CO_3	SiO_2 ppm
					(m equ. l^{-1})							
19.1.72		80	50	9.06	19.6	.295	2.83	11.1	30.6	1.80	5.30	1.1
29.1V.72	3.375		19	8.06	39.1	.249	4.30	8.75	33.8	1.80	6.20	8.7
26.V.72	3.04	40	6.7	8.37	29.1	.321	4.15	7.92	29.4	1.69	7.93	1.0
21.V11. 72	2.595		3.4	8.45	17.8	.521	2.92	11.34	35.0	2.09	8.21	0.9
18.V111.72	2.460	30	6.5	8.57	17.75	.385	2.87	11.42	34.9	2.04	7.51	0.5
15.1X.72	2.56		15	8.49	18.3	.560	2.80	12.5	21.8	1.91	7.96	0.8
14.X.72	2.75	30	23	8.70	22.1	.384	3.53	13.4	24.6	2.20	8.64	2.6
9.X1.72	3.10		13	8.73	21.0	.389	3.76	14.2	26.3	2.04	9.54	0.2
7.X11.72	3.19	40	80	9.70	22.6	.346	3.23	14.8	32.2	2.09	6.37	2.0
4.1.73	3.45		39	9.73	24.1	.356	5.38	13.6	36.0	2.09	4.00	4.7
2.11.73	3.55	60	56	9.31	26.5	.382	4.35	14.0	38.2	2.30	3.48	12.0
1.111.73	3.555	80	38	8.62	25.3	.446	2.97	11.9	35.1	3.61	5.90	11.5
27.111.73	3.765	70	51	8.68	28.4	.485	3.21	14.9	34.9	2.72	8.62	14.5
30.111.73	3.750	70	67	8.37	27.7	.436	3.12	14.6	36.2	2.68	8.53	12.9
27.1V.73	3.440	100	53	8.37	23.2	.415	3.23	15.2	32.1	2.54	8.70	14.5
26.V.73	2.51	80	54	8.26	18.0	.392	2.90	10.8	23.5	2.60	6.81	15.4
11.V1.73	3.55	60	25	7.82	24.0	.421	3.21	13.6	34.6	2.92	6.61	15.7
22.V1.73	3.82	70	56	8.23	24.7	.420	3.51	14.6	35.8	2.47	7.52	14.9
21.V11.73	2.945	40	42	8.42	20.6	.250	3.00	12.9	27.4	1.33	7.12	11.9
16.V111.73	2.955	40	49	8.50	23.5	.520	3.16	8.80	26.1	1.29	7.52	10.7
3.1X.73	3.160	50	53	8.36	23.6	.530	3.20	14.3	28.8	1.26	8.44	9.4

FIGURE 1V.2 : CHEMICAL CHANGES IN GRANTON LAGOON,

1972 - 1973.


20 250
Si O2 ppm
TURBIDITY J.T.U.
0 0
(e)
SiO2
TURB.
1·0
·6 0
·4 0
0
ANIONS
(d)
Cl
HCO3
SO
·8 0
0
CATIONS
(c)
Na
Mg
Ca
K
PROPORTIONS
(b)
100 10
0 COLOUR Pt u.
PH
6
PH
COL.
HORIZONTAL BARS: mean monthly rainfall (max. 100mm.)
4 60
1 30
D± meq/l
W+
Σ+
(a)
D±
1972
1973

early 1967.

$D^{\pm}$ (Fig. IV.2.a) was high after the winter rains of 1972, and fell during the summer, and during a later dry period. Rises were evident during or after the wettest months. These changes were of the general form expected of a water receiving geologically-derived ions during the wet months. Stoichiometric changes were largely due to (compensating) proportionate changes in magnesium and sodium (Fig. IV.2.c) and chloride and bicarbonate (Fig.IV.2.d). At no time did the carbonate ion contribute significantly to total alkalinity.

pH (Fig. IV.2.b) was high early in 1972 and 1973, and low during the winter periods, as is normal (see Chapter 1). The marked rise in pH of early 1973 was accompanied by a relative rise in calcium concentration, and corresponding fall of alkalinity which resulted in a short-term increase of the calcium/alkalinity ratio from about 0.45 to about 1.2. Photosynthesis was probably most intense at that time, the turbidity increase (Fig. IV.2.e) being associated with a marked colour change in the water from grey-green to a bright dark green. Hence photosynthetic utilization of CO_2 probably explains the alkalinity fall, while calcium may have been redissolved from sedimented $CaCO_3$ in the presence of respired CO_2 at the bottom. Yasin (1967) recorded some comparable but erratic changes in pH during 1967.

Changes in colour (Fig.IV.2.b) were more recognisably seasonal than for any other parameter and this suggests that colour was unrelated to hydrology; perhaps it was generated by aquatic organisms responding to light intensity, or by a seasonal decay of biologically-derived material. The summer intensification of colour was not simply an effect of the rise in pH.

Silica concentration (Fig.IV.2.e) was low during 1972 and much higher in 1973. A minimum occurred in late winter of each year. The greatest change in silica concentration coincided with the pH rise of late 1972, and so may have been a biological effect.

The ratio of sodium concentration to that of chloride is similar for all waters in Tasmania (Buckney and Tyler, 1973a and unpublished*). In Granton Lagoon,

* See appendix for summary.

the mean value was 0.45, and the variation small. The highest value occurred at the time Σ^+ was highest (April, 1972), the lowest value occurring in July, 1972. The high value perhaps indicates the preferential leaching of sodium from the catchment during the rains of that period. This may have been a pulse effect.

In the formulation of a model for an "ideal" lake in Chapter 1, it was inferred that pH might be simply related to Σ^+ and that a stoichiometric parameter (i.e. D_-^+) might be related to the negative or inverse of a function of Σ^+. The data for Granton Lagoon are similar to those expected of the "ideal" lake on only nine consecutive occasions (June 1972 to March, 1973); this is mainly a concentrating period.

The best linear fit of pH plotted against Σ^+ (Fig. 1V.3) is:

$$pH = 0.08\Sigma^+ + 5.72; \quad r = 0.748, \; n = 9, \; \Sigma^+ \text{ in m.equ } l^{-1}$$

Clearly, the points in Fig. 1V.3 could be better fitted by a curve or, alternatively, (and perhaps more realistically) admitting to a line of smaller slope and attributing the high pH values to a biological effect.

During the same period, there was no discernible relation between D_-^+ and Σ^+, apart from a vague correlation ($r = 0.42$) between log D_-^+ and $(-\Sigma^+)$. Changes in cation and anion proportions (Fig. 1V.2) are not always all in the same direction relative to seawater. In part, this may be due to the effect that primary producers have on alkalinity, and to selective leaching of salts from the catchment (i.e. pulse phenomena). Under those circumstances, it is expected (Chapter 1) that D_-^+ would be related to the rate of change of flow or of concentration.

The data allow the estimation of a mean rate of change of Σ^+ ($\frac{\Delta\Sigma^+}{t}$) and of mean values of Σ^+ (Σ^+_{mid}) and of D_-^+ (D^+_{-mid}) for some time between successive samples (t is the period in days between samples). Figure 1V.4 shows a plot of $\frac{\Delta\Sigma^+}{t}$ against D^+_{-mid} for the period June 72 - March 73. If the mean rate of change of Σ^+ is an adequate representation of the flow regime for the water body, then this result confirms the supposition made in Chapter 1 concerning the flow regime effect discussed by Dvihally and Vagas (1970).

FIGURE 1V. 3 : REGRESSION OF pH ON Σ^+ FOR GRANTON LAGOON, JUNE 1972 - MARCH 1973.

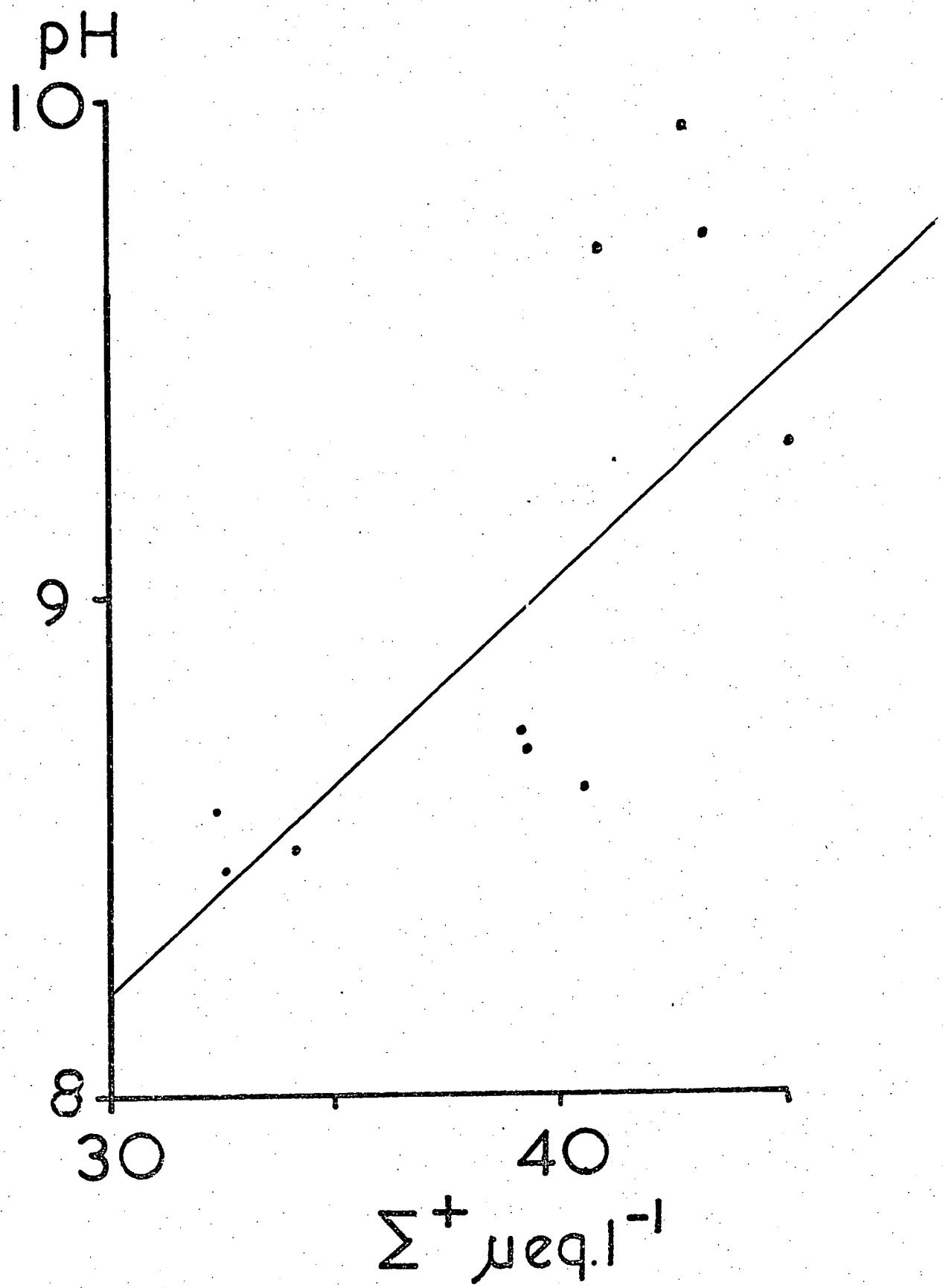
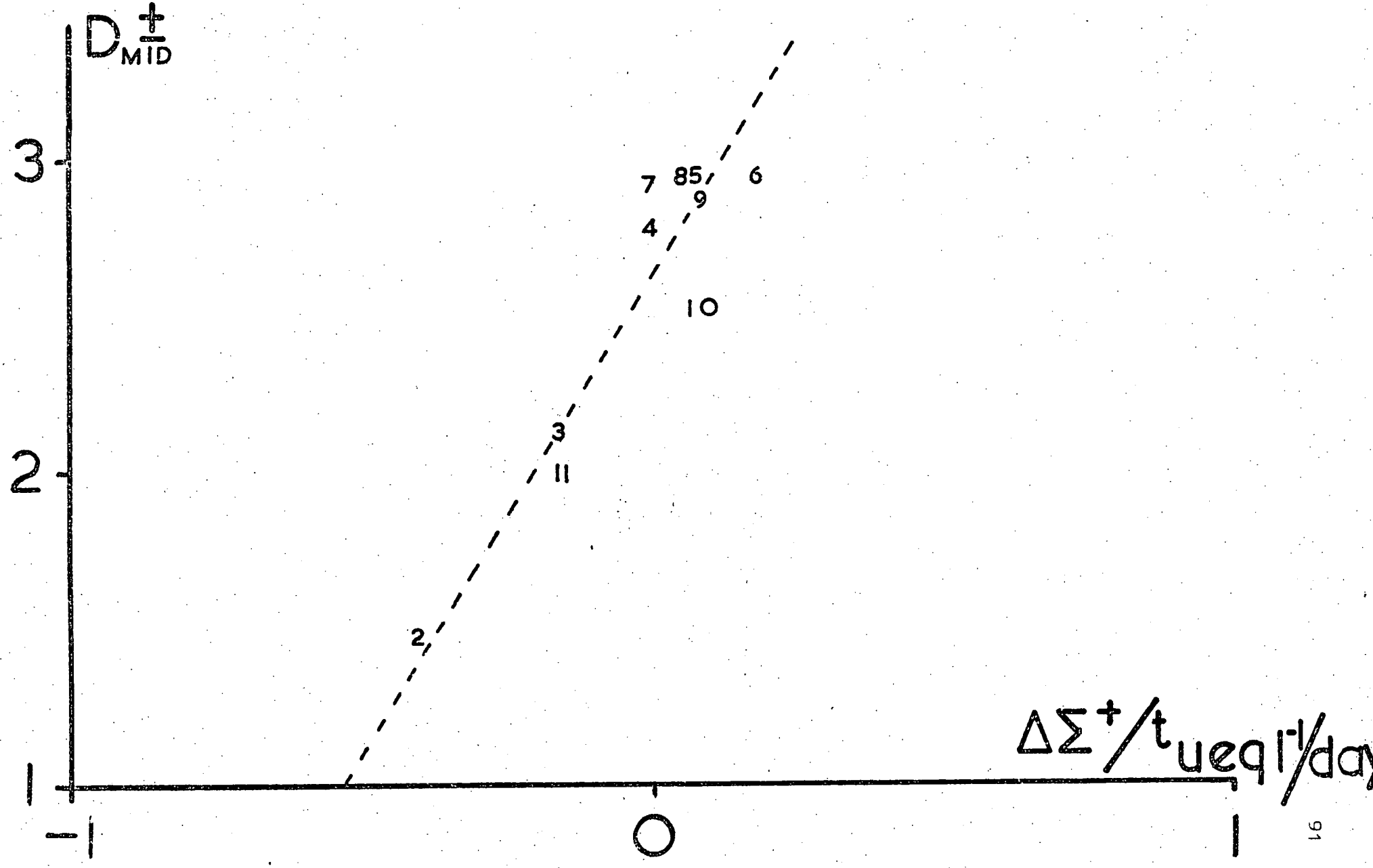

pH
10
9
8
30
40
$\Sigma^+ \mu eq.l^{-1}$

FIGURE 1V.4 : VARIATION OF $D_{\pm}^{+}$ AS A FUNCTION OF THE MEAN RATE OF CHANGE OF TOTAL CONCENTRATION IN GRANTON LAGOON, JUNE 1972 - MARCH 1973. Numbers refer to chronological sequence of samples.


$D_{MID}^{\pm}$
3
2
1
7
85
9
6
4
10
3
11
2
$\Delta\Sigma^{+}/t_{ueq}$ l^{-1}/day
−1
0
1

The following two equations have been found to best describe the relation between D^{+}_{-} and Σ^{+} for the entrie sample period.

$$D^{+}_{-}{}_{mid} = 0.29 \frac{\Delta \Sigma^{+}}{t} - 0.08 \Sigma^{+}_{mid} + 6.45; \quad r = 0.96, \; n = 10$$

$$\text{and} \quad D^{+}_{-}{}_{mid} = 0.21 \frac{\Delta \Sigma^{+}}{t} - 0.06 \Sigma^{+}_{mid} + 5.14; \quad r = 0.70, \; n = 14$$

Chemically, the lagoon seems to oscillate for long periods between the two states represented by the equations. This partitioning of the relationships might be a consequence of the fact that there are two means by which Σ^{+} can increase or decrease: simple evaporative concentration and dilution by runoff, or pulse increases and decreases. No pulses were obvious in the present study, though Yasin (1967) recorded such an effect.

4. CONCLUSIONS

1. The total concentration of ions in Granton Lagoon decreased during and after heavy rains.

2. Stoichiometric changes were mainly the result of compensating proportionate changes between sodium and magnesium among the cations and chloride and alkalinity among the anions. The most discernible changes were related to rainfall; there was a stoichiometric displacement away from seawater following the winter rains, and towards seawater late in the summer periods.

3. pH decreased during the wet part of the year and rose markedly during the early summer months. A turbidity increase during the early summer was associated with a distinct change of colour of suspended material to dark green suggesting that biological control of pH was occurring.

4. Colour intensity showed a marked seasonal variation, being high in summer and low in winter, there being no obvious correlation between colour intensity and pH.

5. Silicon concentration behaved much as did Σ^{+} for part of the study. The summer period initiated a rise of Si concentration to a value which decreased only gradually during the following winter.

6. The sodium to chloride ratio roughly increased and decreased with total

concentration. The calcium/alkalinity ratio remained relatively constant, but temporarily attained a high value which coincided with the pH rise.

7. During the concentrating period of summer, it was possible to demonstrate the existence of a correlation between pH and Σ^+. During the same period, there was evidence that stoichiometric displacement from seawater was related to the rate of change of concentration.

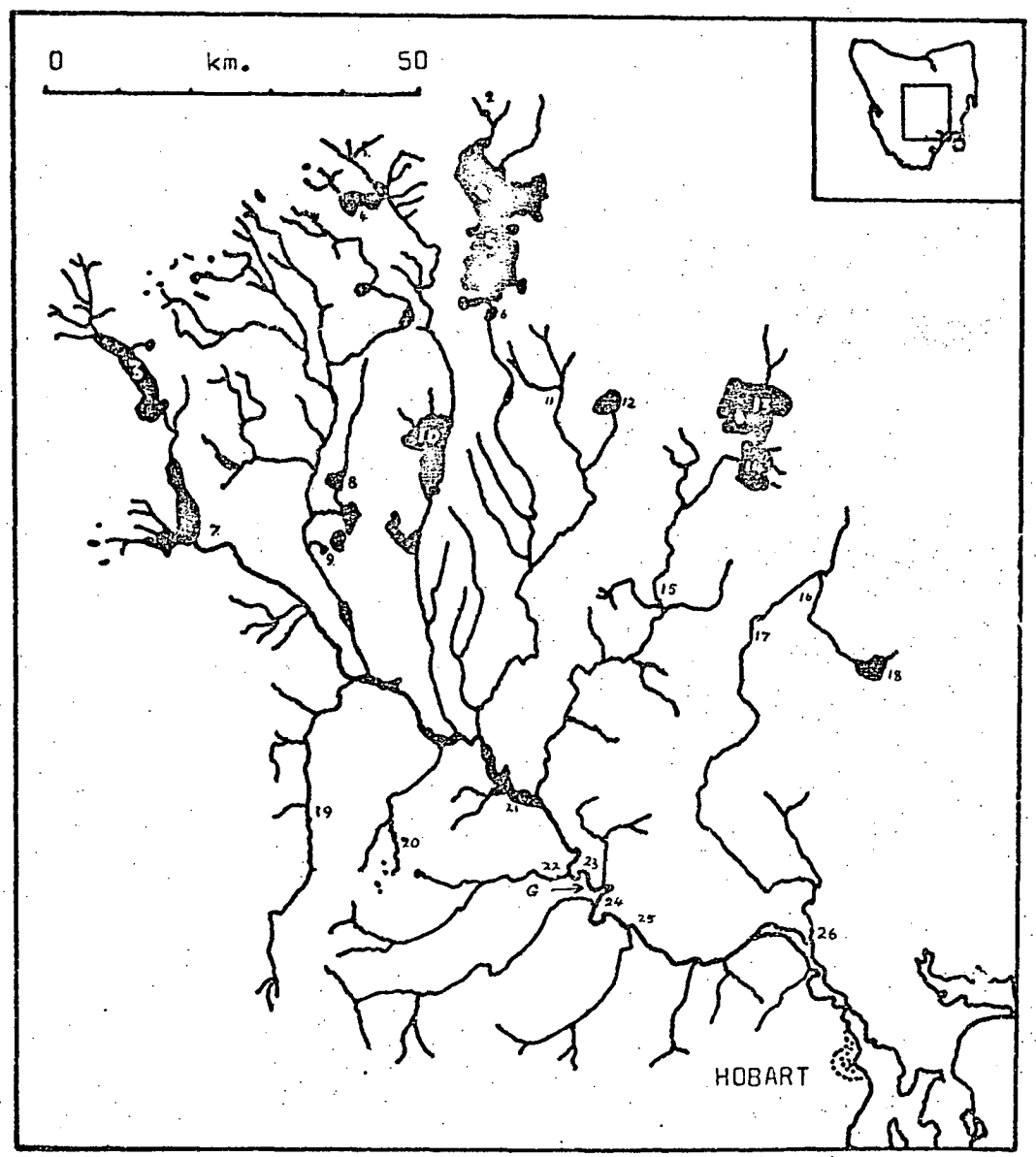
8. D^+_- could be related to total concentration and the rate of change of concentration by two similar equations, which are taken to indicate the probable existence of a flow-regime control on stoichiometry.

FIGURE 1V.5 THE DERWENT RIVER CATCHMENT.

Sample sites:-

1. Ouse R.
2. Pine L.
3. L.St.Clair
4. L. Augusta
5. Great L.
6. Shannon Lagoon
7. Tarraleah Canal
8. Bronte Lagoon
9. Tungatinah Lagoon
10. L. Echo
11. Ripples Creek
12. Lagoon of Islands
13. L. Sorell
14. L. Crescent
15. Clyde R., Bothwell
16. Jordan R., Jericho
17. Jordan R., Apsley
18. L. Tiberias
19. Florentine R.
20. Russell Falls R.
21. L. Meadowbanks
22. Styx R.
23. Derwent R., Bushy Park
24. " " Plenty
25. " " New Norfolk
26. Jordan R., Pontville

G: River Guaging Station, Macquarie Plains



PART 2 THE CHEMISTRY OF THE DERWENT RIVER

1. INTRODUCTION

There is little information on chemical changes in Tasmanian rivers (Tyler and Buckney, 1973), though several single samples have been analysed (Buckney and Tyler, 1973a; Williams, 1964). This report is on chemical variability in the Derwent River during 1972-73.

The Derwent River rises at about 1300m on the Central Plateau (Fig. 1V.5) and flows about 150 km to the south and east where estaurine conditions are established. The catchment upstream of Granton is 95 km^2 in area and consists of Jurassic dolerite in the high areas and various Tertiary rocks (basalts and lake and terrestrial sediments) at lower altitudes (Spry and Banks, 1962). Mean rainfall ranges from about 180 cm yr^{-1} on the plateau to about 50 cm in the south and east. River flow averages about 130$m^3 sec^{-1}$ and is regulated for hydro-electric power production.

2. RESULTS

Chemical data for waters in the catchment are summarised in Table 1V.3 and Fig. 1V.6. Table 1V.4 contains chemical data for the Derwent River at Plenty (site 24, Fig. 1V.5); relative ionic proportions for this site are shown in the ternary diagram (Fig.111.2). The hydrological and chemical changes are presented in Figure 1V.7.

3. DISCUSSION

(A) The Catchment

Waters draining the Central Plateau (samples 1-14) are all dilute except Lagoon of Islands (12) which is abnormal (see Chapter 111 and Buckney and Tyler, 1973a). Lowland tributaries are more concentrated than most highland waters, though some from the west are quite dilute. The most saline tributary, the

TABLE 1V.3 MAJOR ION CHEMISTRY OF WATERS IN THE DERWENT CATCHMENT

Analyses refer to single samples or to means of a number of samples.
Sample Nos. refer to those in Fig. 1V.5

SAMPLE NOS.	K18 /uScm^{-1}	Colour Pt Units	Turbidity J.T.U.	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3	SiO_2 ppm
					/u equ. 1^{-1}							
1.	16.9	-	0.57	6.90	69	4	66	57	59	19	163	1.0
2.	13.1	-	0.52	6.33	74	4	28	33	90	15	65	1.2
3.	21.6	-		6.2	78	5	50	42	113	13	64	2.9
4.	18.04	-	1.4	6.56	65	11	66	41	121	26	87	3.9
5.	21.2	-	8.9	6.86	86	7	62	60	82	22	151	4.3
6.	38.6	-		7.3	96	8	135	184	140	38	281	7.1
7.	27.4	15		5.5	96	17	32	23	230	18	104	2.9
8.	31.0	-		7.1	74	13	290	75	181	74	209	5.1
9.	35.1	-		7.2	83	10	115	83	138	44	230	5.1
10.	28.6	-		7.2	78	14	90	83	92	48	125	3.9
11.	35.3	-		7.4	96	14	131	70	48	11	456	9.6
12.	180	10	7.5	7.70	474	48	724	679	641	47	1463	10.1
13.	52.1	-		7.17	176	27	154	137	270	74	272	11.3
14.	60.9	-		7.16	202	12	172	163	294	94	282	2.2
15.	181	20		7.5	530	45	750	467	1045	17	1550	9.6
16.	2800	10	10.2	8.02	14570	208	8900	12167	31100	2500	3761	6.5
17.	1446	15	1.2	8.08	6830	869	3370	6400	10980	2600	4017	10.6
18.	862	70	1.1	7.31	3826	128	3650	4000	6010	104	3901	8.2
19.	373	-	0.68	8.20	278	14	3550	479	326	35	4087	7.7
20.	42.8	-	1.4	7.21	191	10	93	117	165	21	292	11.3
21.	78.3	30	9.2	7.54	348	18	200	278	377	33	603	5.6
22.	38.6	150	4.5	6.92	205	10	137	159	198	42	239	2.5
23.	53.0	40	2.3	7.18	226	23	173	158	293	28	383	
24.	59.7	20	2.7	7.39	236	11	227	184	258	33	432	4.8
25.	59.9	30	5.1	7.20	237	13	208	179	232	26	409	
26.	798	50	12.0	7.69	4260	136	2330	2750	5000	2245	3386	8.0

FIGURE 1V.6 : RELATIVE IONIC PROPORTIONS FOR WATERS OF THE DERWENT CATCHMENT.

Numbers refer to sample sites in Figure 1V.5.

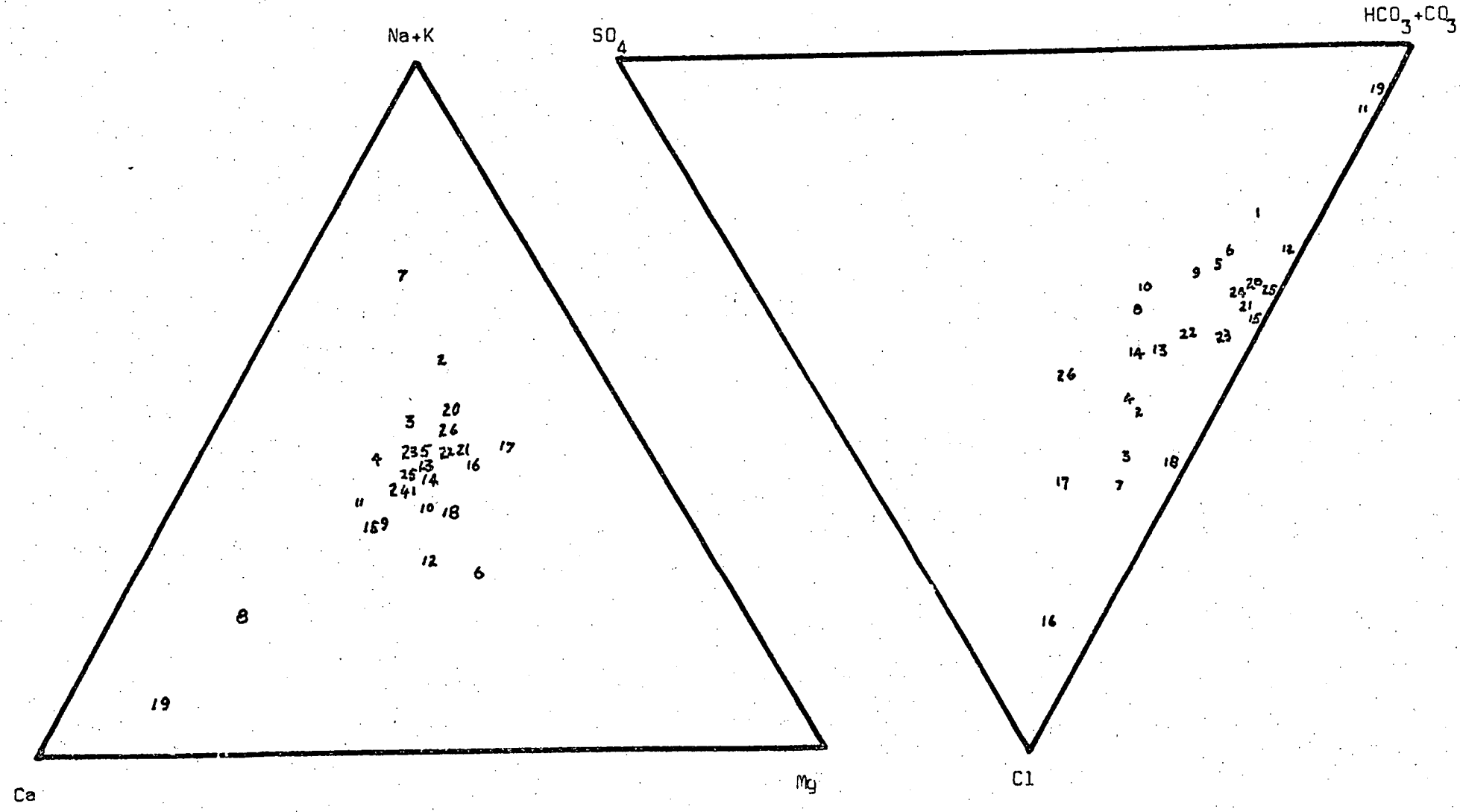

Na+K
Ca
Mg
SO4
HCO3+CO3
Cl

TABLE 1V.4 WATER CHEMISTRY OF THE DERWENT RIVER AT PLENTY

Date	K18 /uScm^{-1}	Colour Pt Units	Turbidity J.T.U.	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3	SiO_2 ppm
					/u equ. l^{-1}							
13.X.71	73.3	30	7.7	7.45	244	10	235	191	218	26	440	
21.V11.72	54.0	30	2.7	6.99	265	12	176	174	315	27	372	6.0
15.XV.72	50.5	20	3.2	7.25	196	10	221	142	238	31	355	5.7
14.X.72	54.0	20	2.3	7.08	230	12	219	176	323	38	322	4.7
9.X1.72	64.4	5	1.1	7.54	192	8	258	167	220	37	473	4.5
7.X11.72	64.0		.95	7.59	189	9	294	200	240	38	531	5.0
4.1.73	60.1	5	1.0	7.64	189	13	239	185	223	38	445	5.0
2.11.73	54.1	15	0.98	7.39	180	14	227	169	218	34	402	3.9
1.111.73	64.7	10	2.5	7.61	197	8	275	202	211	43	565	5.1
30.111.73	60.2	30	1.3	7.55	207	9	262	188	220	39	487	4.2
27.1V.73	56.2	30	5.0	7.28	529	16	160	249	603	53	378	6.7
26.V.73	57.2	40	4.2	7.27	239	6	189	169	233	41	408	6.1
22.V1.73	62.1	20	3.1	7.40	221	12	233	183	255	34	462	2.5
21.V11.73	55.0	30	3.6	7.25	217	9	180	165	249	27	391	2.9
16.V111.73	67.8	20	3.2	7.47	323	9	249	165	269	26	496	4.7
19.1X.73	54.1	10	3.7	7.18	248	12	188	173	229	26	388	5.1
19.X.73	56.6	20	1.8	7.39	202	11	200	170	208	23	449	4.3
20.X1.73	71.9	20	2.0	7.61	234	14	289	221	253	25	461	5.4
13.X11.73	53.3	20	1.5	7.39	179	8	219	165	181	25	378	4.3

Jordon River, is semi-permanent and discharges into the estuary.

At high altitudes, stoichiometry is varied, some of the small creeks and artificial lakes (e.g. 1, 6, 8, 9, 11, Fig. 1V.5) showing considerable geochemical enrichment (Fig. 1V.6). The Florentine River (19, Fig. 1V.5) drains limestone and is dominated by calcium and bicarbonate. Low altitude waters invariably show a larger degree of geochemical enrichment than most of the high altitude waters.

(B) Changes in the Main River

June to August, 1972 and April to June 1973 were periods of abnormally high and variable flows (Fig. 1V.7a). After August 1972 Σ^+ rose erratically, with a marked maximum appearing during the high flows in 1973 (Fig. 1V.7b). At that time, $D^{\pm}$ fell sharply but rose thereafter; low values of $D^{\pm}$ in 1972 also seem to have corresponded with the periods of high flow. Stoichiometric changes reflect almost solely the compensating proportionate changes in sodium and calcium and chloride and bicarbonate concentrations (Fig. 1V.7.c,d).

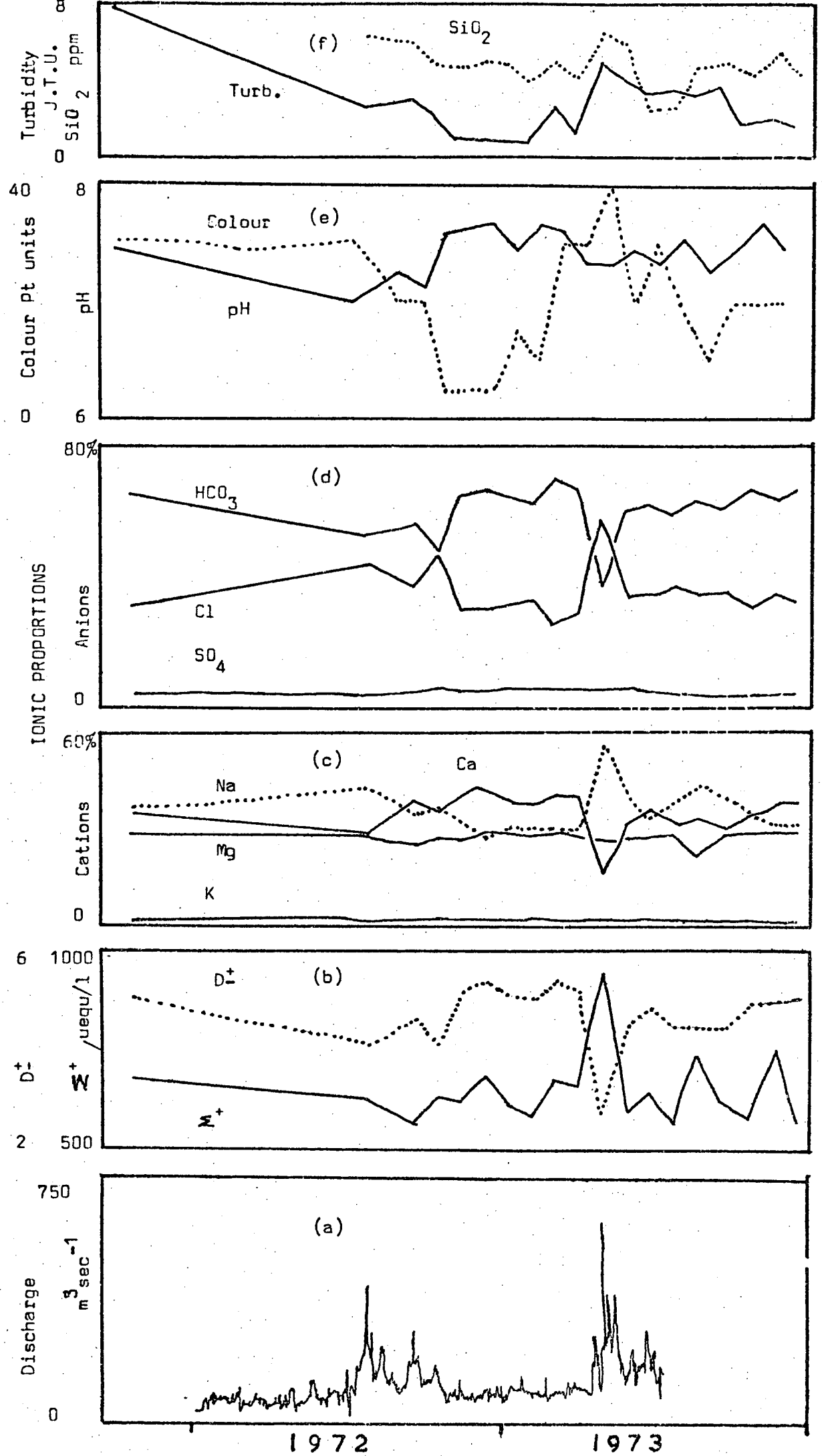
Colour (Fig. 1V.7.e) was highest during the flood periods and lowest at the ends of the winter months; a rise during the summer period was evident.

Despite the smallness of variations in pH, it is possible to recognise that high values were maintained during the summer, and somewhat smaller values during the winter (Fig.1V.7.e) as is usual.

Turbidity and silicon concentration (Fig. 1V.7.f) were high during the period of greatest flow in 1973 and somewhat lower at other times. A net fall of turbidity accompanied a net rise of silicon concentration after the 1973 flood.

The most marked chemical changes were associated with the high flows of 1973:
colour and Σ^+ rose substantially, $D^{\pm}$ fell, and SiO_2 concentration and turbidity were high. These features are characteristic of the pulse discussed in Chapter 1.

FIGURE 1V.7 : VARIATION OF DISCHARGE AND CHEMICAL CONDITIONS IN THE DERWENT RIVER AT PLENTY, 1972 - 1973.


8
Turbidity J.T.U.
SiO2 ppm
0
(f)
SiO2
Turb.
40
8
Colour pt units
pH
0
6
Colour
(e)
pH
80%
IONIC PROPORTIONS
Anions
0
(d)
HCO3
Cl
SO4
60%
Cations
0
(c)
Ca
Na
Mg
K
6
1000
D+-
ueqv/l
W+
Σ+
2
500
(b)
D+-
750
Discharge
m3 sec-1
0
(a)
1972
1973

Apart from the effect of the high flows, there was a general stability of Σ^+ and $D^{\pm}$ which appears similar to the affects of soluble rocks (Grimshaw and Hudson, 1970; Otsuki and Wetzel, 1974). As noted for Granton Lagoon, colour changes were least apparently related to hydrology.

The equation of Leopold et al (1964) relating total concentration to discharge applies only weakly to the accessible data for Σ^+ and discharge (R, in $m^3 sec^{-1}$). Other parameters are better correlated to discharge and the correlations are summarised in Table 1V.5 for which an equation of the general form:

$Q = aR^b$ is assumed (Q is the value of the parameter considered, a and b are constants).

The equations (Table 1V.5) are not applicable in all cases to the high flow period of 1973. At that time, Σ^+, sodium, magnesium, chloride and sulphate concentrations were higher than the regression equation defined, while potassium and silica concentrations, $D^{\pm}$ and pH were lower; calcium and bicarbonate were unaffected. Edwards (1973) recorded similar, though not identical anomalies during the first storm runoffs in some Norfolk rivers.

While flow rates are not high, the normal chemical behaviour for the Derwent River can be summarised as follows for increasing discharge:

(a) The concentrations of sodium, potassium, chloride, and silica rise;

(b) the concentrations of calcium, magnesium, bicarbonate and sulphate fall;

(c) total concentration and pH fall;

(d) stoichiometric displacement towards seawater occurs.

At very high flows (greater than about $1000 m^3 sec^{-1}$) the seawater order of ionic dominance would occur ($Na > Mg > Ca > K$: $Cl > SO_4 > HCO_3$), while at very low flows (less than about $0.01 m^3 sec^{-1}$) the equations define a water with the world average freshwater ionic dominance order (Livingstone, 1963) ($Ca > Mg > Na > K$: $HCO_3 > SO_4 > Cl$). The evidence available here suggests that the ionic proportions of the two standard waters would not be attained by the respective ions at precisely the same flow rates. It is almost certainly invalid to extrapolate

TABLE 1V.5

Coefficients, (a) and exponents (b), of daily mean discharge (R) in m^3 sec^{-1} relating chemical parameters to discharge in the Derwent River at Plenty.

r is the correlation coefficient

* indicates correlation significant at 95% level

o indicates data for flood omitted (one point)

Parameter	a	b	r
Σ^+ / u equ l^{-1}	730	-0.032	0.352 o
Na "	115	0.133	0.733 o *
K "	9.60	0.009	0.158 o
Ca "	547	-0.195	0.705 *
Mg "	242	-0.070	0.471 o
Cl "	123	0.153	0.694 o *
SO_4 "	58	-0.107	0.531 o
HCO_3 "	949	-0.176	0.683 *
SiO_2 p.p.m.	1.41	0.419	0.601 o *
pH	8.79	-0.039	0.873 *
$D^{\pm}$	8.45	-0.122	0.806 o *

the equations to the degree stated, but the extrapolations serve to illustrate the net direction of stoichiometric changes occurring in the river.

The equations allow the estimation of the annual discharge of each ion for the river during the sample period. They are for

sodium	20700	tonne yr^{-1}
potassium	1600	"
calcium	19360	"
magnesium	8470	"
chloride	38000	"
sulphate	690	"
bicarbonate	103800	"
silica	44500	"
total	237120	"

4. CONCLUSIONS

1. The waters of the Derwent catchment range from very dilute in the high rainfall areas of the central Plateau and west to concentrated in the more arid area of the south and east.

2. Stoichiometrically, the water of the river tends to become dominated by geologically - derived ions in the lower reaches.

Discharge in the river was low and somewhat uniform for most of the study period; a flood occurred in each year of study and was characterised by (i) a high concentration of dissolved salts stoichiometically more similar to seawater than the low flow solution and (ii) higher than usual colour, turbidity and silica concentrations, characteristics of a pulse effect.

3. Flow rate (R) during most of the period defined stoichiometric and other parameters (Q) with reasonable surety, the general equation

$Q = aR^b$ being applicable.

4. Total concentration and the concentrations of sodium, magnesium,

chloride and sulphate were higher during the flood than the above equation defined; other parameters were lower, with the exception of pH and alkalinity and calcium concentrations which were not significantly different from those values predicted by the quations.

5. Extrapolation of the equations to very high flows resulted in the definition of a water stoichiometrically similar (not identical) to seawater, while extrapolation to very low flows defined a water stoichiometrically like (not identical to) the world average freshwater.

6. The total discharge of dissolved matter in the Derwent River amounts to about 237,170 tonne yr^{-1}.

PART 3 - THE PHYSICAL AND CHEMICAL LIMNOLOGY OF LAKE DOBSON

1. INTRODUCTION

Previous limnological studies in Tasmania have dealt with tectonic or artificial lakes (Cheng and Tyler, 1973a; Croome and Tyler, 1972; Tyler and Buckney, 1974). This paper deals with physical and chemical aspects of Lake Dobson, a small cirque lake on the Mt. Field Massif at an altitude of 1033m. This area receives a high rainfall (about 170 c.m. per year). The location, bathymetry and major features of the catchment are shown in Figure 1V.8.

Lake Dobson was fertilized ten times between Oct. 1950 and Jan. 1952 by the deposition of bags of fertilizer as described by Weatherley and Nicholls (1955).

2. RESULTS

(A) PHYSICAL

Morphometric data are summarised in Table 1V.6. Rainfall and hydrological figures are presented in Figure 1V.9(a); flow data are estimates based on the discharge recorded at the Lake Fenton guage (Fig. 1V.8) and assume that the discharge per unit area is the same for both catchments. (The mean flow obtained for Lake Dobson was 2790 m^3 day^{-1} which is comparable to the figure of 3400 $m^3 day^{-1}$ obtained by Weatherley and Nicholls, 1955). Surface and bottom temperatures for the lake are shown in Figure 1V.9.(b).

(B) CHEMICAL

Chemical data for water from the surface and 0.5m from the mud near the deepest point are collected in Tables 1V.7 and 1V.8 and summarised in Figures 1V.10 and 1V.11. Means and standard deviations of cation concentrations and some other parameters for the interstitial water in the sediments are contained in Table 1V.9. Some difficulty was experienced in identifying the surface layer of mud in the

FIGURE IV.8 : LOCATION, BATHYMETRY AND CATCHMENT OF LAKE DOBSON.

Lakes: 1. Dobson

2. Eagle Tarn

3. Fenton

4. Seal

5. Webster

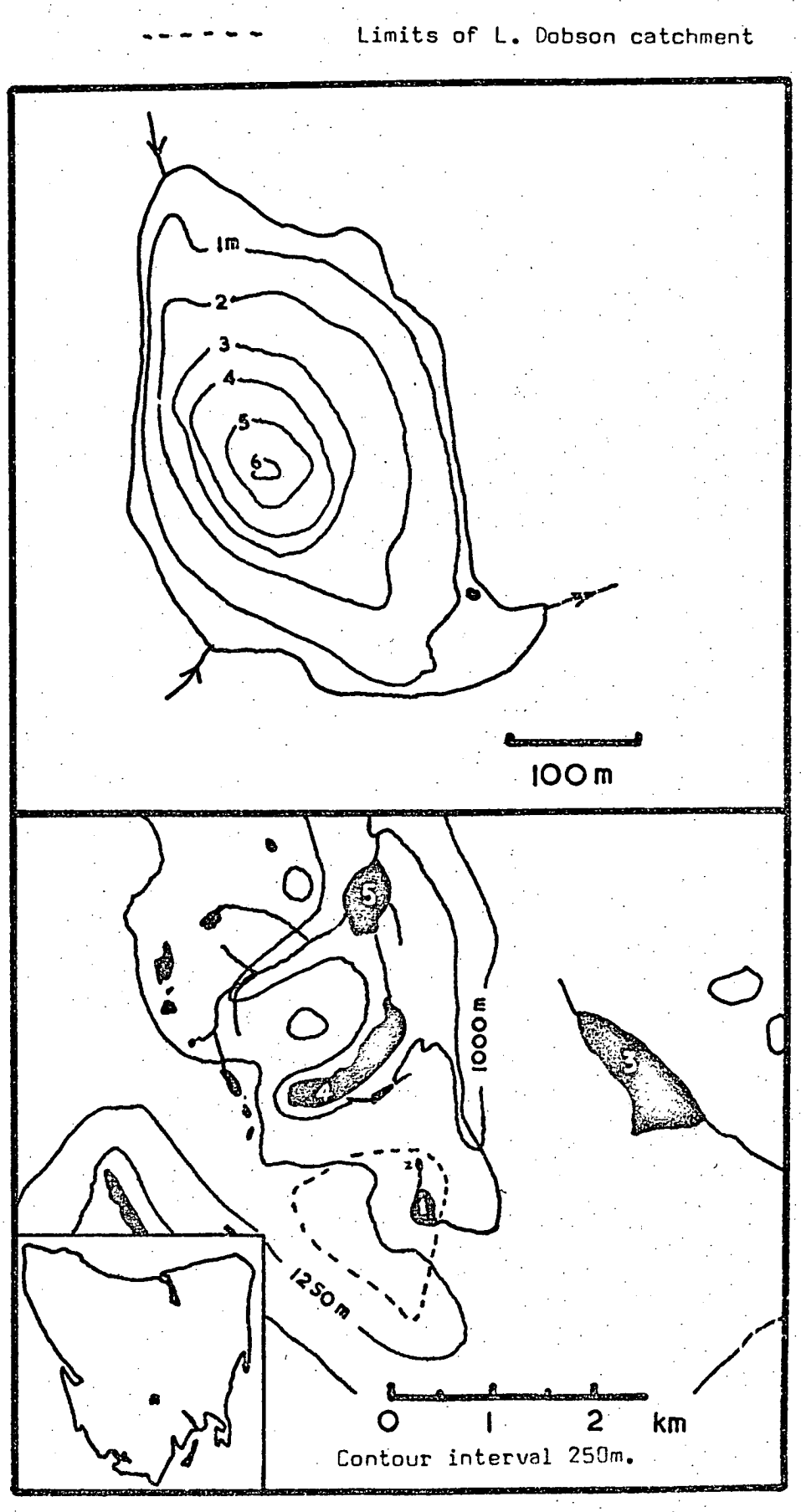

Limits of L. Dobson catchment
1m
2
3
4
5
6
100 m
5
4
1000 m
5
1250m
0 1 2 km
Contour interval 250m.

TABLE IV.6

MORPHOMETRIC DATA FOR LAKE DOBSON

Catchment area (ha)	101.9
Surface area (ha)	8.25
Lake Volume (m^3)	1.64×10^5
Perimeter (m)	1140
Max. Length (m)	431
Max. Depth (m)	6.1
Mean Depth (m)	1.99
Shoreline Development	1.12

FIGURE 1V.9 : CHANGES IN (a) ESTIMATED RUNOFF AND (HISTOGRAM) MONTHLY RAINFALL AND (b) WATER TEMPERATURE IN LAKE DOBSON, 1972 - 1973.

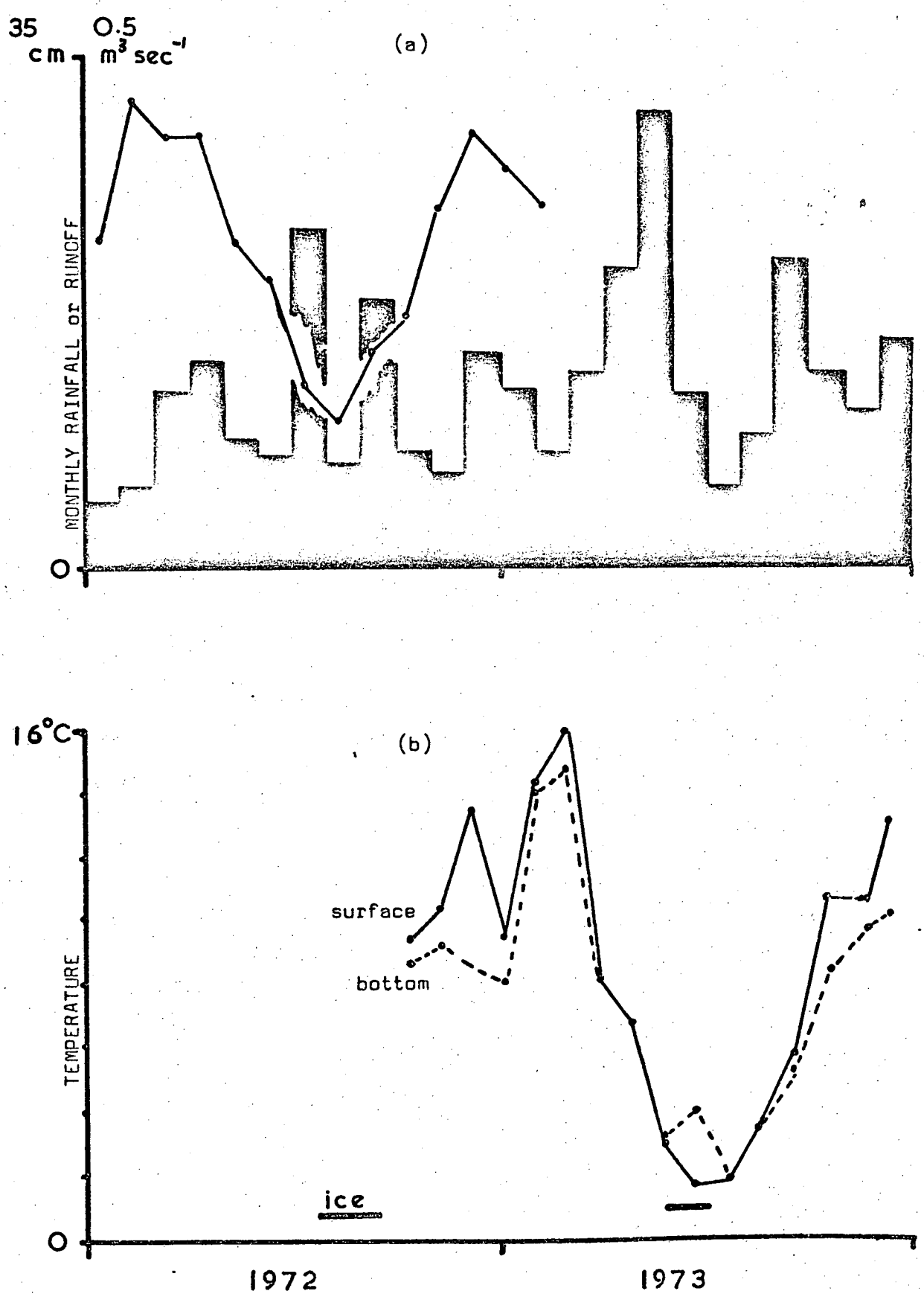

35
cm
0.5
m³ sec⁻¹
(a)
MONTHLY RAINFALL or RUNOFF
0
16°C
(b)
surface
bottom
TEMPERATURE
ice
0
1972
1973

TABLE 1V.7 MAJOR ION CHEMISTRY OF LAKE DOBSON - WATER AT THE SURFACE

DATE	K18 μScm^{-1}	Colour Pt Units	Turbidity J.T.U.	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3	SiO_2 ppm
					μ equ. l^{-1}							
13.X.71	26.9	-	.45	7.03	85	3	81	83	98	22	132	
19.1.72	33.1	-	.42	7.02	104	9	88	124	88	33	204	7.8
4.11.72	35.0	-	.31	7.36	102	7	68	127	83	31	191	7.6
28.11.72	41.2	-	.50	7.36	113.	13	100	134	88	31	261	7.5
1.1V.72	34.0	-	.41	7.36	111	7	104	141	116	40	207	7.4
29.1V.72	33.5	-	.44	7.33	104	3	96	122	129	33	183	6.7
8.V.72	33.6	-	.37	7.22	117	3	96	123	128	36	175	8.5
26.V.72	29.9	-	.39	7.16	135	15	47	100	120	35	142	9.7
14.V1.72	33.2	-	.36	7.17	126	15	48	92	132	31	260	7.9
25.V1.72	33.3	-	.48	7.12	129	13	51	93	95	34	280	9.0
13.V111.72	34.3	-	.46	7.05	104	6	96	109	119	33	256	6.7
18.V111.72	32.6	-	.34	7.05	103	6	97	108	110	31	254	8.0
15.1X.72	31.0	-	.48	7.10	103	9	117	92	118	32	226	6.8
14.X.72	33.0	-	.46	7.03	110	5	75	116	161	33	222	8.4
9.X1.72	35.5	-	.38	7.05	104	5	108	119	111	29	225	7.9
17.X1.72	31.4	-	.38	7.31	101	4	105	118	107	29	289	4.9
7.X11.72	35.4	-	.34	7.34	103	11	109	148	128	30	348	8.6
4.1.73	35.2	-	.27	7.30	118	8	106	148	133	30	272	6.7
2.11.73	36.8	-	.40	7.27	109	11	102	140	132	28	269	6.8
1.111.73	37.5	-	.35	7.21	118	9	121	135	129	37	302	7.0
30.111.73	32.8	-	.48	7.45	125	7	115	128	122	32	281	6.5
15.1V.73	33.7	-	.42	7.22	116	5	91	123	122	30	269	7.7
27.1V.73	25.7	-	.63	7.05	105	6	67	90	121	29	187	6.5
26.V.73	26.6	-	.43	7.12	103	5	81	93	106	28	192	6.9
22.V1.73	20.4	-	.38	6.96	82	5	70	79	93	23	163	4.6
21.V11.73	20.4	-	.54	7.23	106	7	98	119	92	16	258	6.3
16.V111.73	29.2	-	.44	7.12	120	3	101	103	107	16	249	6.7
19.1X.73	28.4	-	.43	7.02	94	6	92	108	102	17	216	4.3
19.X.73	31.7	-	.57	7.34	119	13	90	118	118	15	257	6.2
20.X1.73	32.3	-	.44	7.37	122	8	98	141	130	17	295	5.6
13.X11.73	32.5	-	.65	7.29	108	10	110	133	100	19	221	6.9

TABLE 1V.8 MAJOR ION CHEMISTRY OF LAKE DOBSON - WATER SAMPLED ½M. FROM THE BOTTOM

Date	K18 μScm^{-1}	Colour Pt Units	Turbidity J.T.U.	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3	SiO_2 ppm
					μ equ. l^{-1}							
13.X.71	34.1	-	.6	7.00	80	1	83	83	127	23	198	
4.11.72	36.3	-	.52	7.13	106	9	67	125	107	31	169	6.3
1.1V.72	39.7	-	.85	7.31	140	10	104	148	138	34	230	7.9
29.1V.72	34.0	-	.76	7.28	110	5	94	124	99	33	221	
26.V.72	30.6	-	.52	7.17	117	11	52	92	110	35	127	8.0
25.V1.72	35.0	-	.65	7.07	122	10	48	92	121	34	260	7.3
18.V111.72	35.8	-	.88	7.03	104	2	106	110	106	35	275	8.4
15.1X.72	30.4	-	.43	7.14	102	5	113	100	116	33	234	9.5
14.X.72	30.8	-	.60	7.11	104	4	92	113	110	32	235	8.4
9.X1.72	34.2	-	.38	7.22	108	5	108	127	129	30	282	7.2
7.X11.72	35.1	-	.33	7.33	99	9	112	146	119	28	311	10.4
4.1.73	35.6	-	.33	7.27	107	7	108	142	149	30	250	5.2
2.11.73	36.3	-	.39	7.17	105	12	110	145	131	26	263	6.4
1.111.73	34.0	-	.41	7.21	112	5	106	123	112	36	223	7.4
30.111.73	32.9	-	.65	7.21	118	3	114	127	118	31	269	7.4
27.1V.73	27.3	-	.71	7.14	96	3	67	95	107	29	192	6.4
26.V.73	26.0	-	.49	6.97	98	3	84	89	103	28	191	7.0
22.V1.73	34.7	-	.47	7.00	95	3	121	130	100	23	331	9.1
22.V1.73	29.7	-	.65	7.11	92	6	99	114	81	15	250	6.2
16.V111.73	29.7	-	.58	7.18	107	1	102	97	97	16	259	7.6
19.1X.73	28.0	-	.62	7.06	94	3	99	111	129	17	226	6.0
19.X.73	29.7	-	.56	7.10	86	4	91	115	99	15	251	6.0
20.X1.73	31.2	-	.53	7.28	102	7	92	130	109	15	283	5.6
13.X11.73	31.4	-	.43	7.25	95	4	105	125	82	19	206	6.9

FIGURE 1V.10 : CHEMICAL CHANGES IN THE SURFACE WATER OF LAKE DOBSON, 1972 - 1973.

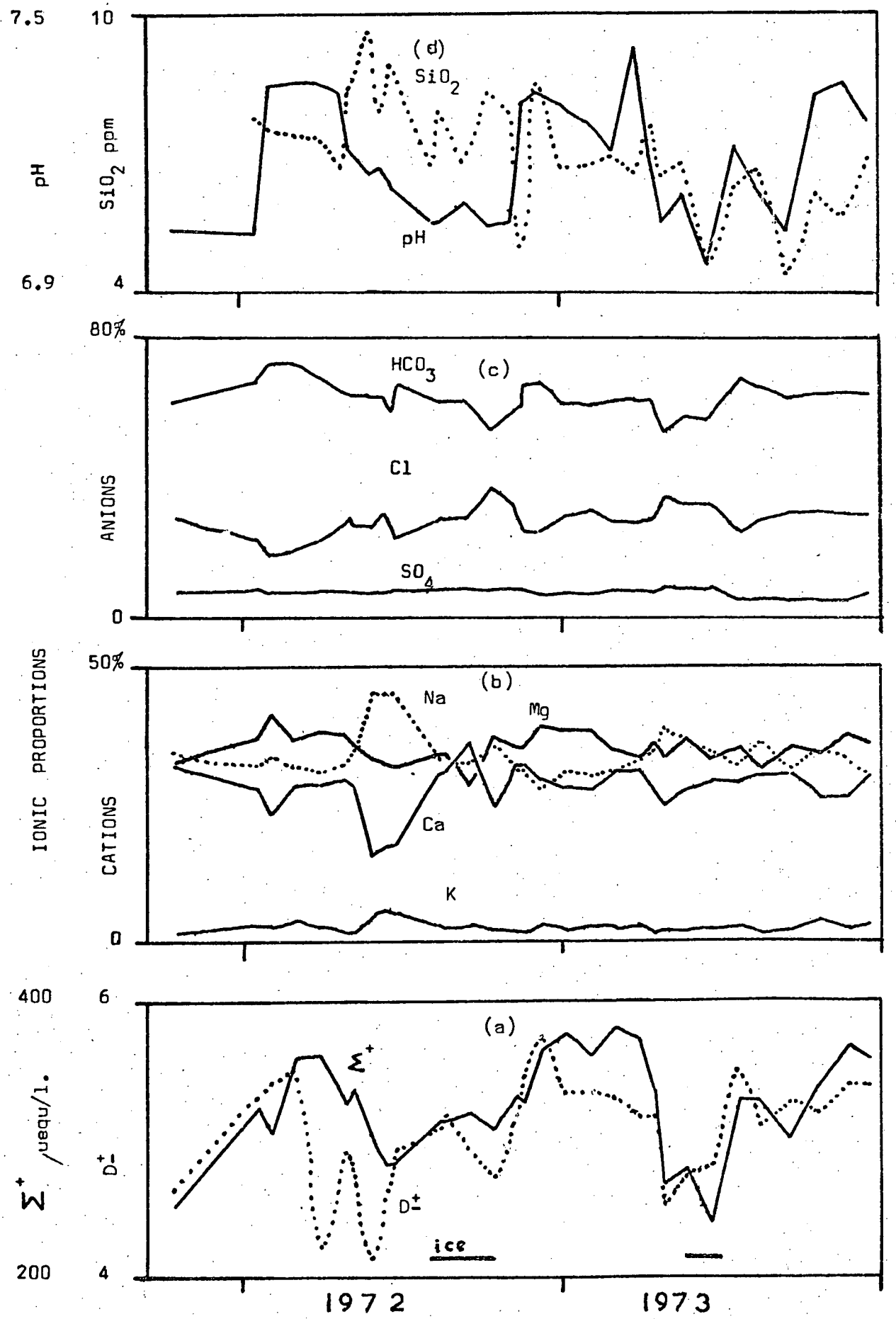
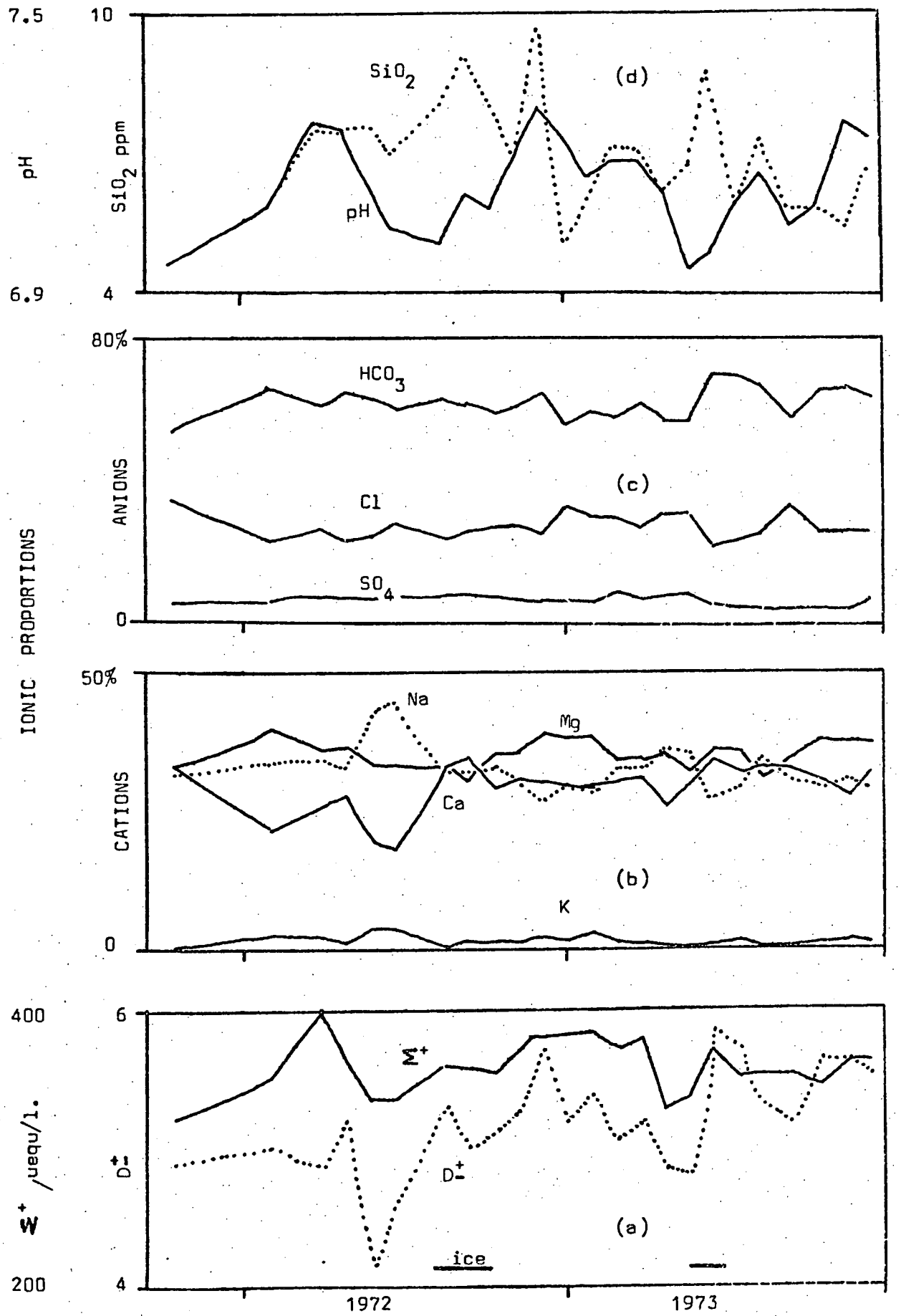


FIGURE 1V.11 : CHEMICAL CHANGES IN THE BOTTOM WATER OF LAKE DOBSON, 1972 - 1973.



Petersen grab. After the iced-over period in 1973, a green film was evident on the mud surface. Most mud samples were taken from about 20cm below the water - sediment interface.

Relative proportions of the major ions are shown in Figure 1V.12.

Throughout the study, the water was quite clear (Turbidity about 0.5 J.T.U.) and saturated with respect to oxygen at the surface. The oxygen probe was allowed to settle in the mud on each sampling; a minimum of 84% of the saturation value was obtained for this surface mud.

3. DISCUSSION

(A) PHYSICAL

Discharge (Fig. 1V. 9a) was least during winter when precipitation was retained in the catchment as snow. Though the greatest rain fall occured in winter, a seasonal variation was obscure.

Water temperature in the lake (Fig. 1V. 9b) ranged between 15.9°C in late summer and 1.3°C in winter; bottom water was colder than the surface water except when the temperature of the latter fell below about 4°C. Up to 5cm of ice covered the lake during the coldest periods. The polymictic status of Lake Dobson was recognised by Weatherley and Nicholls (1955).

(B) CHEMICAL

Variation of total concentration (Fig. 1V.10a) appears to have been abnormal. High values of Σ^+ were recorded during summer when runoff (Fig. 1V. 9a) was high. The same general behaviour could be observed for the bottom water (Fig. 1V.11a), though the changes were smaller - a relatively high concentration being maintained over the two years.

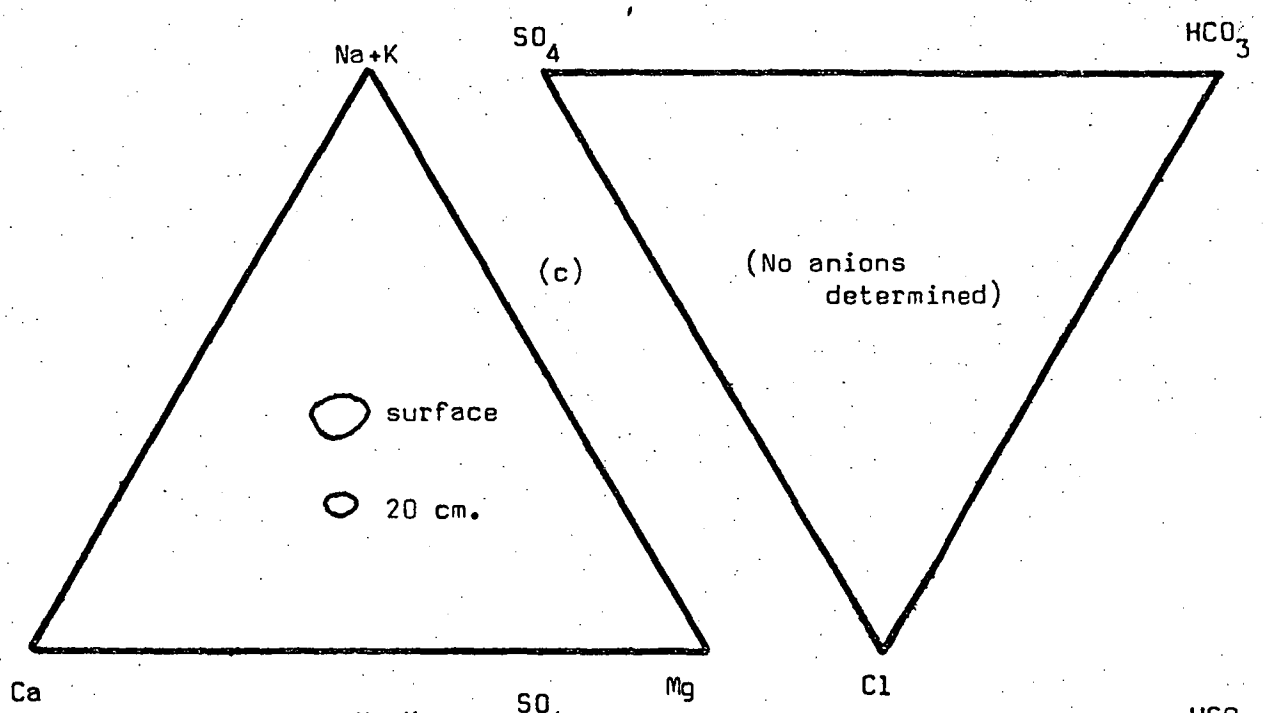
Stoichiometrically, the lake water was most different from seawater during summer (when runoff was high). This pattern is probably normal (see Chapter1). Changes were the same throughout the lake, though the bottom water varied more erratically than the surface water though perhaps less extensively. All cations

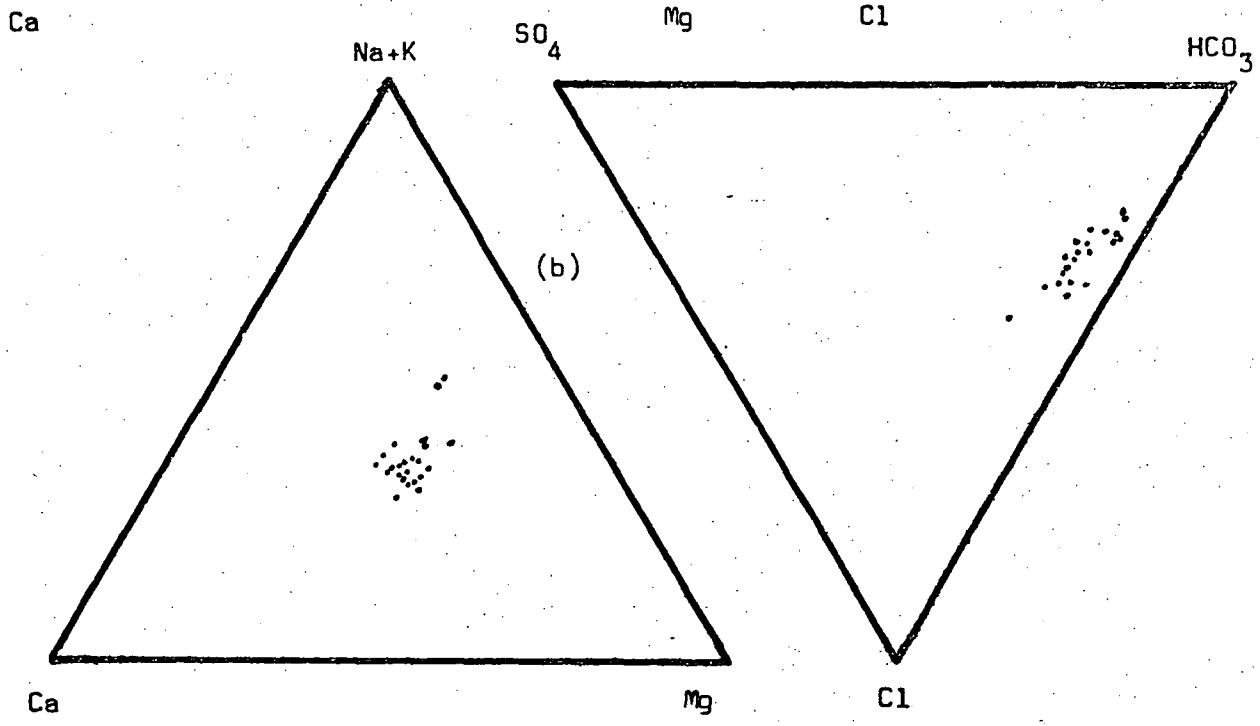
FIGURE IV.12 : RANGE OF RELATIVE IONIC PROPORTIONS IN LAKE DOBSON;

(a) SURFACE WATER

(b) BOTTOM WATER

(c) SEDIMENT INTERSTITIAL WATER.


Na+K
SO4
HCO3
(c)
(No anions
determined)
surface
20 cm.
Ca
Mg
Cl


Na+K
SO4
HCO3
(b)
Ca
Mg
Cl

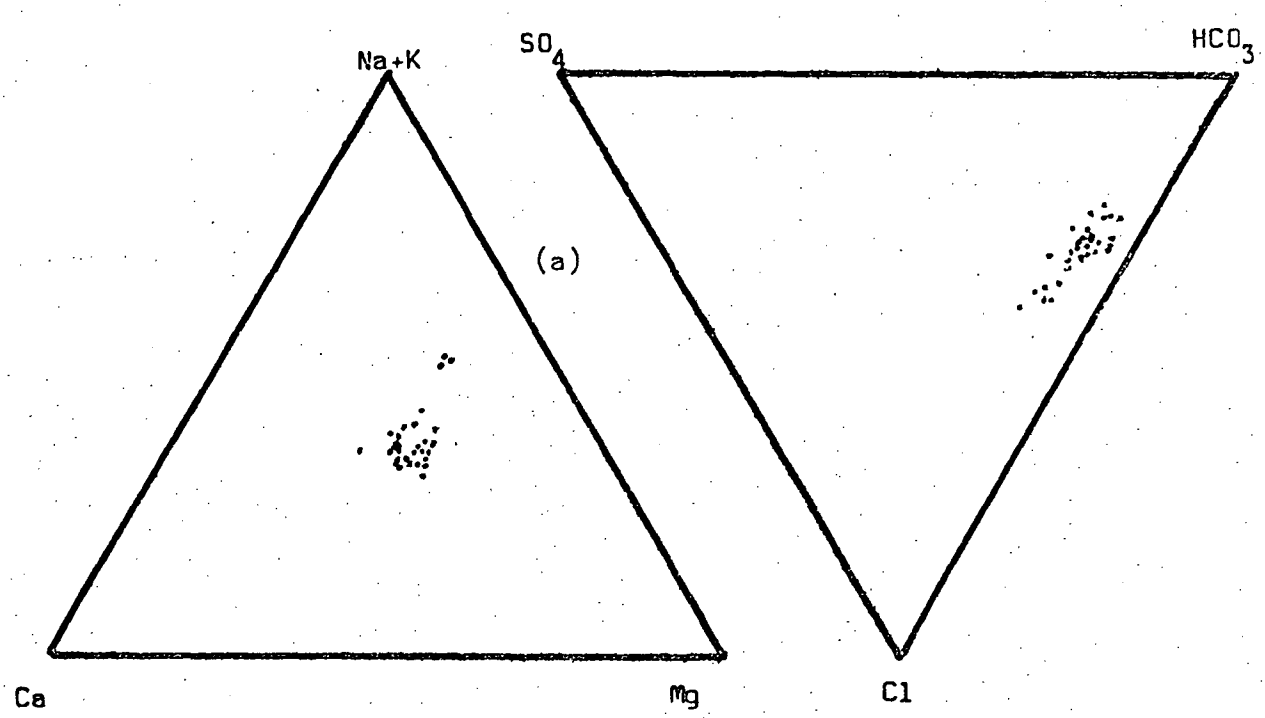

Na+K
SO4
HCO3
(a)
Ca
Mg
Cl

TABLE 1V.9

Means and (in parentheses) standard deviations of chemical characteristics of interstitial water from the mud of Lake Dobson.

Depth in mud (cm. Approx)	Na	K	Ca	Mg	$^{+}$	pH	SiO_2	Fe	Mn
	(proportions of $^{+}$)				/uequl^{-1}		p.p.m.		
0	.321 (.073)	.042 (.017)	.356 (.064)	.281 (.032)	367.7 (36.0)	7.15 (.297)	11.63 (2.40)	- -	- -
20	.241 (.015)	.022 (.007)	.408 (.036)	.330 (.036)	519.9 (28.3)	7.15 (.124)	15.9 (4.45)	8.77 (3.73)	.608 (.434)

proportions displayed some variation (Figs. 1V.10b, 1V.11b) while sulphate proportion remained relatively constant (Figs. 1V.10c, 1V.11c).

The relative chemical stability of the bottom water is further evidenced by pH changes (Figs. 1V.10d, 1V.11d). Overall, pH showed a marked tendency to be highest during the summer. An increase of pH occurred in winter, 1973 when ice covered the lake. During the summer, pH was lower in the bottom water than in the surface water.

Silica concentrations (Figs. 1V.10d, 1V.11d) changed erratically; a net dilution was evident in the surface water over the study period.

The major cation chemistry of the sediment interstitial water was relatively constant for the deeper muds (Table 1V.9). and more variable for the upper muds. The interstitial water was enriched in silica, potassium, calcium, and sodium relative to the overlying water. In the surface mud, mean magnesium concentration was absolutely and relatively lower than in the overlying water. This suggests that magnesium was leached from the sediments more completely than other ions. Silica concentration in the interstitial water was higher than in the lake water; mean pH values were about the same for both. Iron and manganese concentrations in the deeper mud water were variable. In view of the oxygenated condition of the surface mud, no marked change of total concentration in that layer would be expected (Mortimer, 1941; 1942).

The estimated discharge (R) for Lake Dobson is related to pH and magnesium concentration according to the equations shown (for the surface water) in Figure 1V.13 and as summarised (for top and bottom water) in Table 1V.10. $\sum^{+}$ is less clearly related to R, and the correlations for all three parameters are less significant for the bottom water. Comparable regressions for other parameters were much more obscure. The equation relating $\sum^{+}$ to R (Table 1V.10) confirms the anomalous observation (above) that total concentration tended to be high when discharge was high.

TABLE IV.10

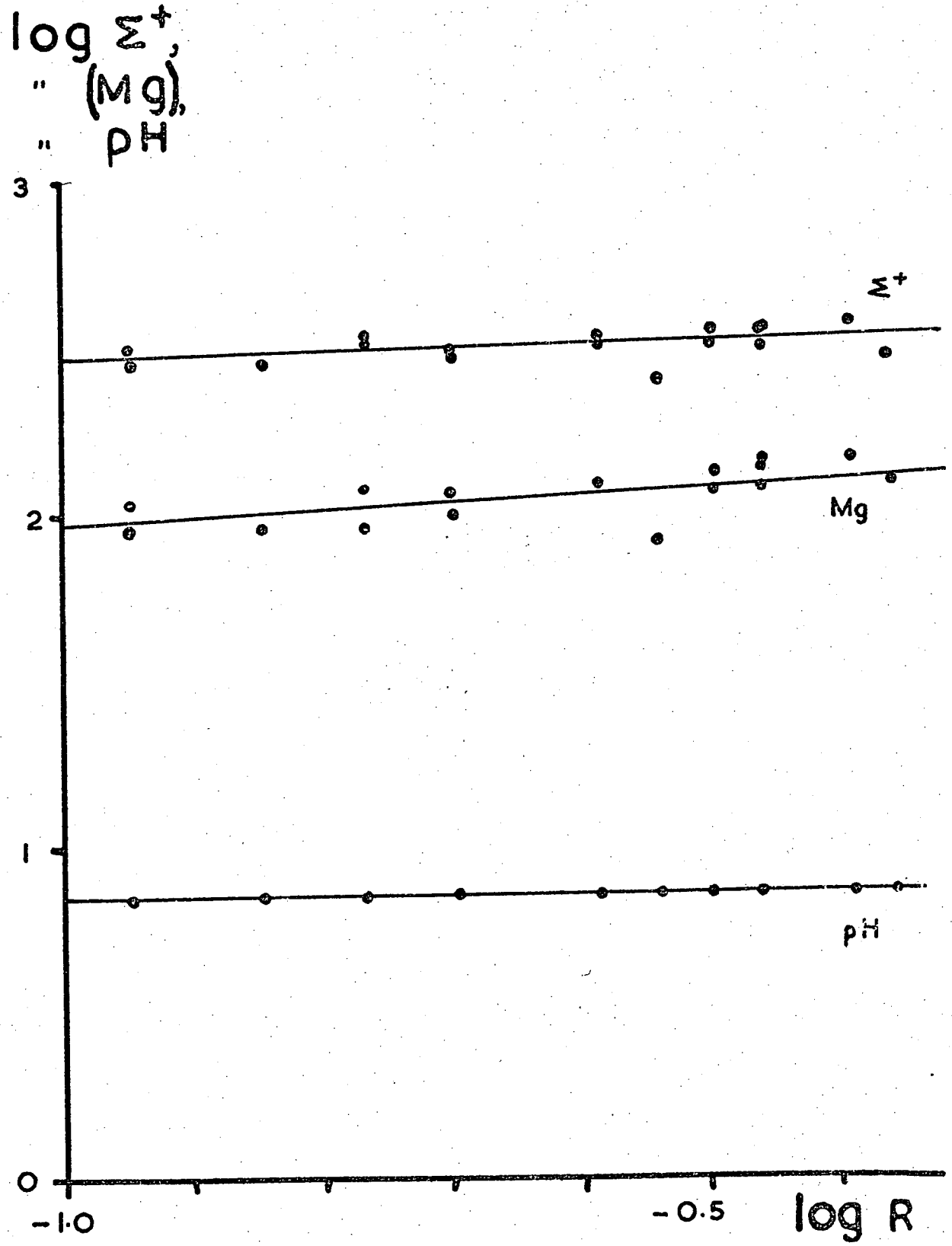
Coefficients, a, and exponents, b, of the estimated discharge, R (in m^3 sec^{-1}), for Lake Dobson; the chemical parameter (P) listed are related to R by an equation of the general form

$$P = aR^b$$

r is the correlation coefficient

Parameter (P)	a	b	r	Significance level
SURFACE WATER (n = 11)				
$^+$ (/u equ l^{-1})	373	0.103	0.439	ca. 90%
Mg (")	165	0.244	0.636	95%
pH	7.51	0.031	0.724	"
BOTTOM WATER (n = 7)				
$^+$ (/u equ l^{-1})	368	0.047	0.344	70%
Mg (")	161	0.231	0.557	95%
pH	7.38	0.019	0.569	"

FIGURE 1V.13 : CORRELATION BETWEEN ESTIMATED RUNOFF AND: TOTAL CONCENTRATION, MAGNESIUM CONCENTRATION AND pH IN LAKE DOBSON.


log Σ+,
" (Mg),
" pH
3
2
1
0
Σ+
Mg
pH
-1.0
-0.5
log R

The inter-sample mean of D^{+}_{-} (D^{+}_{-} mid) is related to the intersample mean of Σ^{+} (Σ^{+}mid) and the mean rate of change of Σ^{+} ($\frac{\Delta\Sigma^{+}}{t}$) by the following equations which are significant at the 95% level:

for the surface water:

$$D^{+}_{-}\ \text{mid} = 0.068\ \frac{\Delta\Sigma^{+}}{t} + 0.005\,\Sigma^{+}\text{mid} + 3.444;\ r = 0.627$$

and for the bottom water:

$$D^{+}_{-}\ \text{mid} = 0.066\ \frac{\Delta\Sigma^{+}}{t} + 0.005\,\Sigma^{+}\text{mid} = 3.656;\ r = 0.455$$

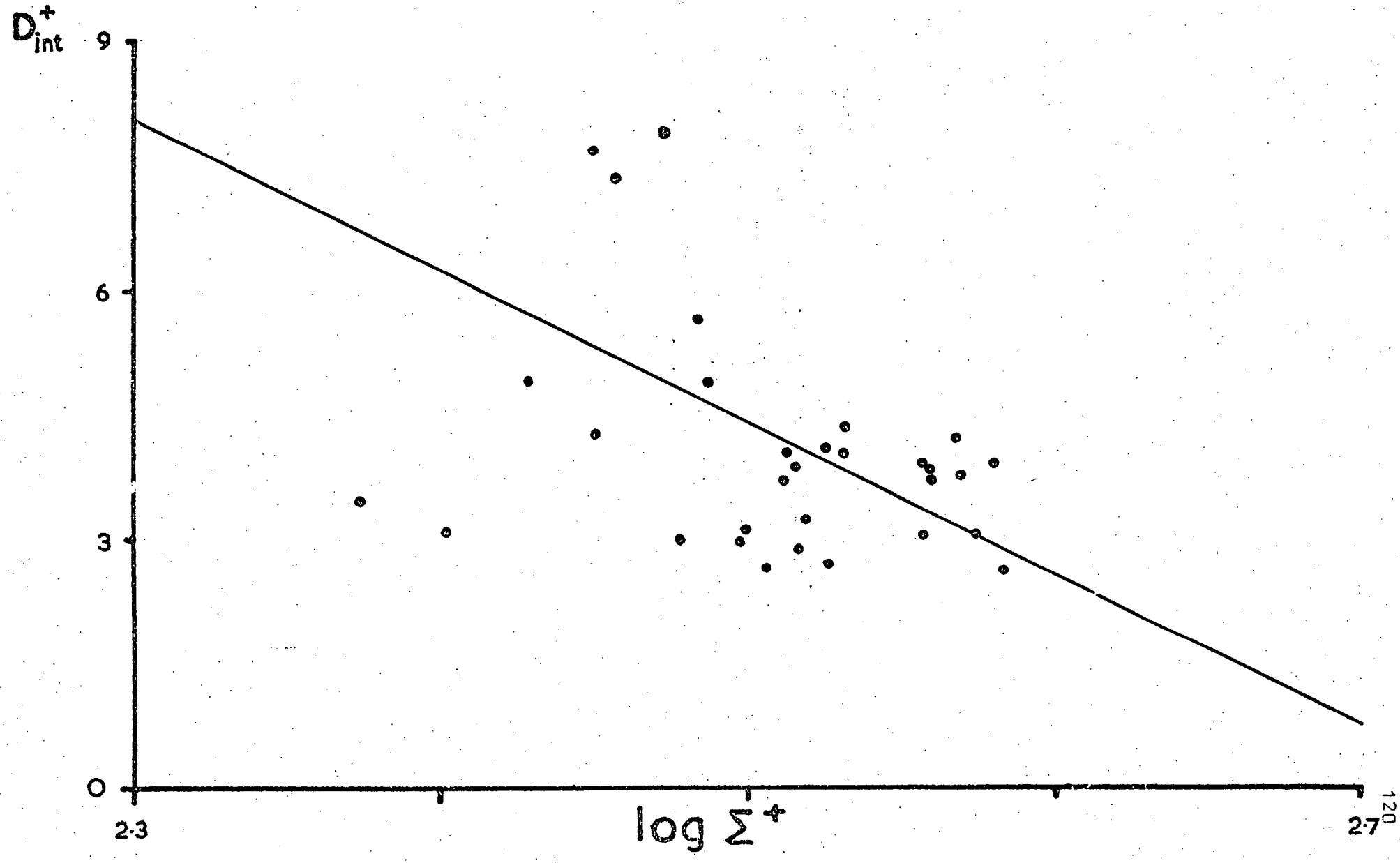
Clearly, the regression is less definitive for the bottom water, though even for the surface water, the equation does little more than account for the main trend of D^{+}_{-} mid.

The observation that Σ^{+} increases with increasing flow is a characteristic ascribed to the pulse effect in Chapter 1. Hence it is reasonable to suspect that there is in the catchment an accumulation of soluble material which can be readily leached away. Since magnesium is the only cation whose concentration showed a dependence on flow rate and whose concentration was also diminished in the surface sediments, the source of this material might be the lake sediments. The slight chemical stability of the bottom water relative to the surface water has already been noted as has the relative obscurity of the regressions investigated. The role that sediments play in determining the chemistry of the overlying water can be quite significant (Lerman and Brunskill, 1971).

(C) THE EFFECT OF THE SEDIMENTS

Lake Dobson water has a higher concentration of dissolved substances than neighboring waters (see Buckney and Tyler, 1973a) with the exception of the very shallow Eagle Tarn (see Chapter 111 and Fig.1V.8). This high concentration could conceivably reflect continued diffusion of salts from the sediment interstitial water in which concentrations of the ions are quite high. It would be expected that as the diffusive input of water from the sediments became more extensive, the stoichiometry of the water would approach that of the interstitial water.

FIGURE 1V.14 : CATION STOICHIOMETRIC DISPLACEMENT FROM THE INTERSTITIAL WATER (D^{+}_{int}) AS A FUNCTION OF TOTAL CONCENTRATION IN LAKE DOBSON.


D^{+}_{int}
9
6
3
0
2·3
log Σ^{+}
2·7

There is a general trend for the cation stoichiometry of the lake water to approach that of the deeper interstitial water (Table 1V.9). The best equation found to describe this trend is:

for the surface water:

$$D^{+}int = 49.8 - 18.2 \log\Sigma^{+};\ r = 0.56,\ n = 31\ (p<0.01),$$

where $D^{+}int$ is the cation stoichiometric distance from the interstitial water, (as derived in Chapter 11). The distribution of points is shown in Figure 1V.14. $D^{+}int$ is most invariable at the high values of Σ^{+}, so that the lake surface water can be viewed as being chemically bufferred at a composition similar to that of the sediment interstitial water. An exponential trend of the same general form best describes conditions in the bottom water, though the regression is less definitive ($r = 0.365$).

The discussion by Lerman and Brunskill (1971) of the diffusion of major ions from sediments indicates that when the concentration of an ion in the lake water attains a value greater than that in the interstitial water, the direction of diffusion is reversed, and that the rate of diffusion of any one ion is proportional to the concentration gradient between the interstitial water and the overlying water. This suggests that the chemistry of Lake Dobson could reflect some balance between the dilution of ions by through-flowing water and their replenishment by diffusion from the sediments. This would go some way towards explaining the anomalous increase of total concentration with increasing flow rate.

Equations of the general form

$c = a\,R^{(xc + y)} + d$ - where c is the concentration of the ion considered R is the flow rate and a,x,y and d are constants - account for the variation of concentration of the main dissolved constituents. The values of a, x, y and d for each of the ions is contained in Table 1V.11. The term $(xc + y)$ is analogous to b in table 1V.12.

TABLE 1V.11

Constants a, x, y and d defining the relationship between ionic concentration, c, and flow rate, R, in Lake Dobson

$$c = a\,R^{(xc + y)} + d$$

Parameter	a	x	y	d
	Surface Water			
Na /u equ l^{-1}	62.559	-0.007	0.676	38.531
K "	0.115	-0.195	0.606	6.286
Ca "	92.355	-0.009	1.033	19.145
Mg "	100.650	-0.007	1.026	46.434
Cl "	70.063	-0.008	0.832	37.427
SO_4 "	26.725	-0.027	0.831	3.522
HCO_3 "	158.340	-0.004	0.809	46.953
SiO_2 p.p.m.	4.141	-0.113	0.770	2.715
	Bottom Water			
Na /u equ l^{-1}	86.112	-0.008	0.817	18.121
K	4.446	-0.176	1.458	2.649
Ca	107.136	-0.008	0.855	4.059
Mg	116.242	-0.007	1.020	23.797
Cl	97.660	-0.008	1.008	29.725
SO_4	14.688	-0.029	0.826	13.841
HCO_3	109.624	-0.004	0.787	87.214
SiO_2 p.p.m.	6.424	-0.109	0.825	0.832

All values of x are negative, and of y positive. These equations indicate that for values of c less than $\frac{-y}{x}$, an increase in R will cause an increase in c, and for values of c greater than $\frac{-y}{x}$, an increase of R will cause a decrease of c. Thus, the equations define values, c_i, of c which are stable with respect to flow rate.

From the above equation it will be obvious that Ci is defined as:

$$Ci = \frac{-y}{x} = a + d.$$

The calculated values of Ci are about the same (usually within 5%) for each of these equations, and for both the surface and bottom water. The mean values are in Table 1V.12.

The equations provide no indication that the various values of Ci are attained at the same value of R, though they suggest that at high values of R, each concentration will be equal to the respective Ci. Thus, Ci can be viewed as the concentration in the overlying water at which the sediments and through-flowing water are maintained in a steady-state condition.

The values of Ci are high for calcium, magnesium and sulphate relative to the concentrations observed in the lake (Tables 1V.6, 1V.7), so that Ci for these ions is rarely attained.

The array of Ci values for the dissolved ions define a water with $\sum^+$; of 363.5 μ equ.l^{-1} and a specified stoichiometry; this stoichiometry can be used as the origin stoichiometry in the construction of D_i^+, the stoichiometric displacement from the steady state stoichiometry.

There is a general trend for D_i^+ to be low and invariable at the higher values of $\sum^+$ (Figure 1V.15), as would be expected from the above considerations. There is a similar general decrease of D_i^+ with increasing flow rate. D_i^+ is greater than zero at all times, and this suggests that the equations identifying Ci are not entirely adequate as a representation of the conditions in the lake. To some extent this would reflect

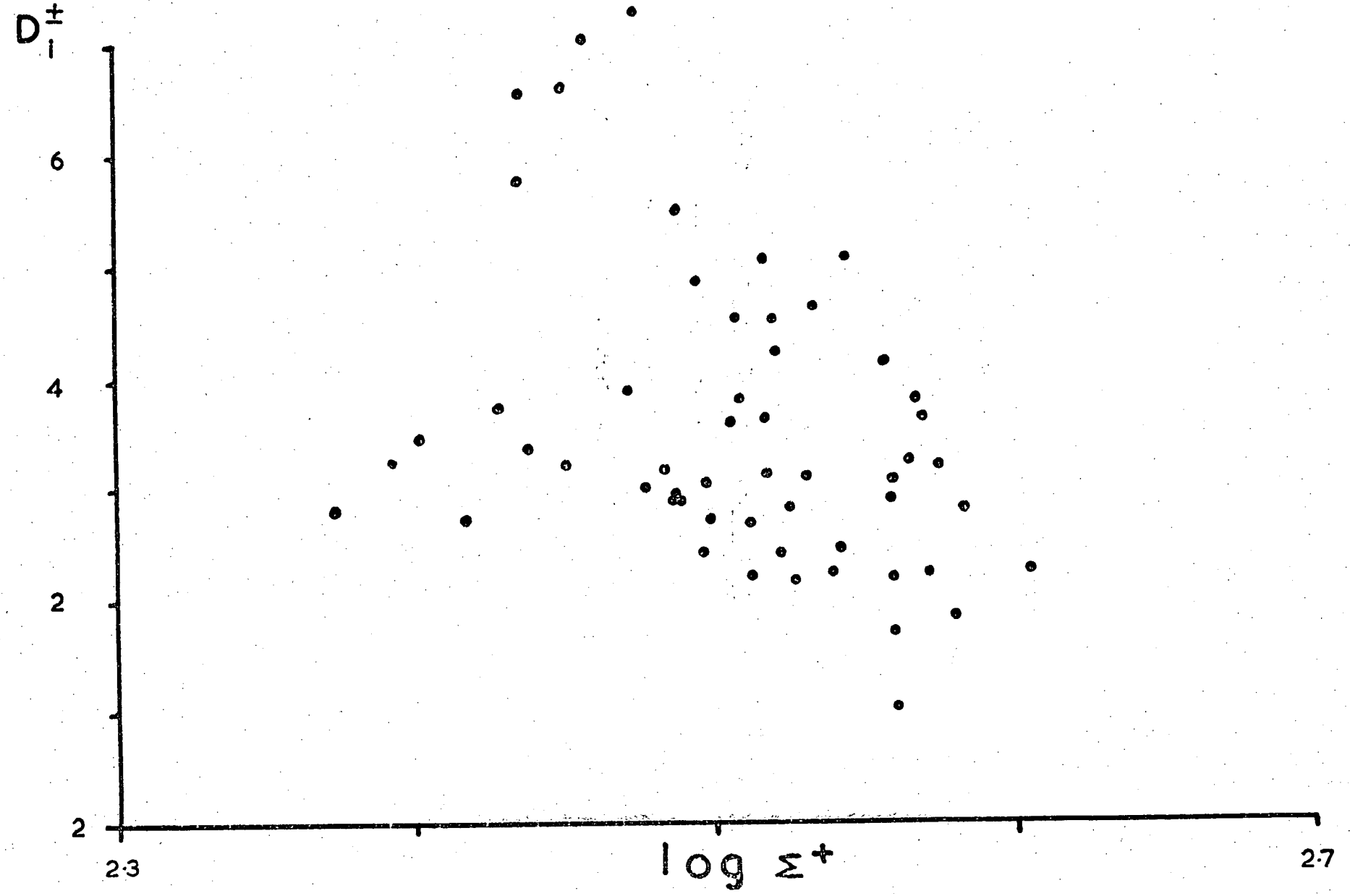
(a) the dependence of diffusion rates on temperature (Lerman and Brunskill,

TABLE IV.12

Mean values of Ci (see text) for Lake Dobson

Ion	Ci (μ equ l^{-1})
Sodium	100.95
Potassium	6.76
Calcium	110.97
Magnesium	144.85
Chloride	116.23
Sulphate	29.50
Bicarbonate	200.29
Silica	7.15

FIGURE 1V.15 : STOICHIOMETRIC DISPLACEMENT FROM THE STEADY STATE COMPOSITION ($D^{\pm}_{i}$) AS A FUNCTION OF TOTAL CONCENTRATION IN LAKE DOBSON.


$D_1^{\pm}$
6
4
2
2
2·3
log Σ^+
2·7

1971),

(b) the contribution of dissolved material from the catchment and

(c) the fact that Ci values are estimates based on simple estimates of flow rate for the lake.

The highest values of Σ^+ and the lowest values of D_i^+ occur at higher temperatures (r=0.713 and 0.456 respectively). This is in agreement with the hypothesis that the diffusion of ions from the sediments is a major source of dissolved material. Nevertheless, the influence of temperature is merely indicated; it is likely that the equations represented in Table IV.11 should incorporate a temperature term (concentrations, c, of all ions are highest at higher temperatures).

4. CONCLUSIONS

1. Lake Dobson is polymictic and nearly saturated with respect to oxygen.

2. An anomalous seasonal variation in runoff results from the retention of water in the catchment as snow during the winter.

3. Water temperature is lowest in winter when ice may form on the surface; during the iced-over period the bottom water may be warmer than the surface water.

4. Stoichiometrically, the lake water differed most from seawater when runoff was high. pH was highest during the summer.

5. The bottom water was somewhat less variable in stoichiometry, pH and total concentration than the surface water; total concentration tended to remain high in the bottom water.

6. High total concentration occurred when runoff was high.

7. The effect of runoff, R, on the concentrations, c, of the major dissolved species is defined by equations of the form:

$$c = aR^{(xc + y)} + d$$

These equations are interpreted as indicating that the Lake attains a steady state chemistry as a result of the interaction of flow rate with the diffusion of ions

from the sediments.

8. The term (xc + y) in the above equation probably reflects a dependence on temperature.

9. The steady state condition is approached when runoff is high; that is, when total concentration is high.

10. Runoff therefore determines the stoichiometry of the Lake Dobson solution.

C O N C L U S I O N

In Chapter 1, the usefullness of a simple scheme of chemical variability based on the proposals of Gibbs (1970) was examined. In a number of respects this scheme was found to be applicable to the published data on chemical variations in inland waters. Thus, a "normal" behaviour might be stated as:

> During wet periods geologically-derived ions become proportionately more important than those derived from the atmosphere; a diminution of total concentration occurs at the same time. Reverse processes occur during dry periods.

Gibbs (1970) did not rate biological influences as important on a survey basis, and it is in this respect that the "normal" scheme is most deficient. Where biological activity is intense, the changes in pH, bicarbonate concentrations and probably other parameters are regulated by the biota.

Vollenweider (1968) reported the early application of changes in alkalinity to the classification of some lakes into trophic classes. The present considerations provide some basis for such an approach, though perhaps a useful chemical indicator of biological activity would be obtained only by considering the alkalinity changes in conjunction with changes in pH, calcium concentration and some other factors (as evidenced by Granton Lagoon, Chapter 1V) and then only in relation to the changes which would normally occur in a sterile system. It is possible that the seasonal change of the diurnal range of these parameters would be a little more useful in this regard.

Saline waters would appear to be distinctive in only one regard: their stoichiometric constancy relative to fresh waters. This invariability is not

absolute and in some particular cases (Blinn, 1971; Kilham, 1971) not recognisable, but in situations where geological influences are not a typical it is the rule. As shown in Chapter 111, the variability of concentration is a function of mean total concentration over a wide range of salinities; this increase in variability of concentration is accompanied by a stoichiometric stabilisation. As biotopes, saline waters are therefore osmotically stressing and variable. The demarcation between fresh and saline waters proposed by Buckney and Tyler (unpublished*) is at a salinity of about 10‰ for waters of near-seawater stoichiometry, which is the salinity recognised by Bayly (1972) as that above which inhabiting organisms are distinctive in terms of osmoregulation and salinity tolerance. As noted in Chapter 11, this is also the salinity at which the highest pH has been observed in Tasmanian waters. Thus, there may be a case for the adoption of 10‰ as the general demarcation between fresh and saline systems.

Pulse phenomena are a further departure from the simple scheme proposed. At least in extreme cases, these seem to result from a particular climatic occurrence, namely the saturation of the catchment after a prolonged dry period. In such circumstances the concentration of ions in solution is probably a function of their solubility. Under more-constantly humid conditions their concentration is more likely to be a function of flow rate and weathering rate.

In a large catchment over which climatic conditions may vary greatly, pulses of small magnitude and restricted origin may contribute to the discharge of dissolved material at most times during the year. This might explain the "abnormal" stoichiometric behaviour of the Derwent River (Chapter 1V), though it is more likely that the rock weathering rate in the catchment is sufficiently slow to ensure that atmospherically-derived ions dominate the runoff at all times.

There appears to be no adequate treatment of the relation between the hydrology and hydrochemistry of pulses in the literature, so this problem is one

which stands out as needing further investigation. The use of the rate of change of total concentration as determinant of stoichiometry (Chapter 1V) has proven statistically acceptable, though it is not as satisfactory as the logarithmic relation between ion concentrations and runoff identified for the Derwent River (Chapter 1V). The behaviour of Lake Dobson (Chapter 1V) bore some similarities to the pulse effect, and equations of the type developed for Lake Dobson might be applicable to pulses.

Round (1971) expounded the idea that the growth of algal populations in freshwaters was regulated by "shock" factors which included the lowering of water temperature and release of nutrients during the overturn in a stratified lake. Pulse effects have many similar features; which include high concentrations of nutrients and of major ions, higher acidity and a stoichiometry which may be very different from the usual composition. Thus, pulses might have a "shock" effect on algal populations.

Climate is by far the most important determinant of variability of total concentration (Chapter111). The geology is at least as important as the climatic pattern in determining the stoichiometric variability of a water. These observations are not contrary to the simple scheme of variability based on the idea of Gibbs (1970).

The results obtained in Chapter 111 suggest the need for caution in nominating morphometric factors as responsible for differences in chemical behaviour between lakes. Only stoichiometric variability is likely to be significantly affected by morphometric factors, particularly the catchment area/ surface area ratio.

Certain other influences, which were not considered important by Gibbs (1970), may be locally important. The effect of vegetation on the water chemistry is probably profound for Lagoon of Islands (Chapter 111) in which higher plants must

play an important (perhaps unique) role in the nutrient and salt cycle for the lake. Vegetation of the catchment can apparently also have a destabilizing influence on the water chemistry - as evidenced by Lake Pedder (Chapter 111 and Buckney and Tyler, 1973b) and Brownwater Lagoon. To some degree, this may reflect the weak retention of excreted substances and bound inorganic ions by the plants under most conditions, so that high flow regimes move a great deal of this material en masse.

Sediments are probably an important stabilising influence in shallow waters such as Lake Crescent (Chapter 111) and in small water bodies - as has been demonstrated (Chapter 1V) for Lake Dobson. Little quantitative investigation of this aspect of limnology has been conducted apart from studies into redox phenomena in the muds. The study of the behaviour of permanently wet sediments can be expected to illuminate some problems of the weathering and release of dissolved material from solids. For Lake Dobson (Chapter 1V) a steady-state relation between supply of major ions from the sediments and their removal by the outflow has been inferred, and (as noted above) this type of relationship might best describe the aquatic chemistry of pulses.

The use of the two-part description of major ion chemistry as described in Chapter 11 has been useful in a number of regards.

First, it has allowed the simplification of the investigation of chemical variability. The distance parameter used obscures the details of stoichiometry without obscuring the broard nature of the stoichiometric difference from seawater.

Secondly, it has aided in the characterisation of a spectrum of chemical types of water. That is, a given set of concentrations of major ions can be shown to occur with a range of values (of another parameter) which in some cases is small. Thus, a classification of waters into similarity classes is both feasible and relevant. This fact suggests that a system concept would be applicable to a description of the chemical features of inland waters.

The clear definition of a geologically-influenced water type was noted in

Chapter 11. While the best-defined water does not correspond with the published composition of the world average freshwater (WAFW), the observed limitations of values taken by nearly all parameters at high values of $D^{+}_{\pm}$ is similar in essence to the observation by Rodhe (1949). There is (of course) no evidence to suggest that the WAFW is an ultimate composition for an evolving aquatic system. Nevertheless there is evidence for the existence of a composition which is well-defined (and probably rarely attained). It is unlikely that this composition does not represent some equilibrium condition. The inferred tendency for the Derwent River (Chapter 1V) to approach a similar composition at low flows - when equilibrium between water and catchment is most attainable - adds weight to this concept. The apparent rarity of this equilibrium condition is good reason to heed the assertions of Gorham (1955, 1968) that water chemistry is more a function of ambient conditions than of a long-term trend towards equilibrium.

The equations obtained for the Derwent River (Chapter 1V) are probably the most useful type recognised. It is possible that in mathematical terms systems could be viewed in terms of their deviation from equations of the form $(X) = aR^{b}$

Thus, for Lake Dobson (Chapter 1V) it was recognised that b was a function of concentration: $b = x\ (X) + y$.

It would be useful to investigate the significance of the terms a and b. The results for Lake Dobson suggest that b is a function of the mobility of the ion concerned under the conditions prevailing in the system. Hence, a pulse might be best analysed by investigating the behaviour of b during a flood period. The term a might be a function of catchment area or of the climatic regime.

Edwards (1973) obtained equations of the same form as those presented for the Derwnet River for some rivers in Norfolk. The nutrient ions nitrate and phosphate showed similar relations to flow rate. Thus, it is possible that much of the investigation presented above for the major ions also applies for nutrient and other ions, though the nutrients (at least) would be subject to biological

restrictions on their mobility. Still, it might prove useful to approach the hydrochemistry of nutrients from an assessment of the behaviour of the major ions.

The simplified scheme of variability proposed in Chapter 1 is not adequate to explain the behaviour of real systems. However, deviations from "normal" behaviour can be ascribed to factors which are locally important, but not recognised (Gibbs, 1970) as being of fundamental significance. Thus, the scheme proposed is at least heuristically useful since it facilitates the identification of locally-important controls on major ion chemistry.

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APPENDIX 1

A summary of the main features of a paper by R. T. Buckney and P. A. Tyler dealing with the chemistry of some of the more concentrated waters in Tasmania. (Manuscript in preparation).

Major ion analyses for the closed lakes of central Tasmania, and for other waters of the sub-humid parts of Tasmania are presented; these complement the survey (Buckney and Tyler, 1973a) which dealt almost exclusively with waters of TDS less than 300 ppm. Some relations between chemical parameters are reassessed for the entire concentration range (about 10 ppm to 20% TDS) found for Tasmania. The following regressions are presented:

$$\log S = 0.962 \log \Sigma^{+} - 1.046; \quad r = 0.999$$

$$\log \Sigma^{+} = 0.957 \log K_{18} + 1.039; \quad r = 0.994$$

$$\log (Na) = 0.978 \log (Cl) + 0.027; \quad r = 0.994.$$

Some morphometric data for these lakes are presented.

Criteria used to delineate fresh from saline waters are discussed, together with some biologically-relevant information. A chemical criterion for distinguishing fresh and saline waters is proposed:
The ratio of the concentration of alkaline earth metals to Σ^{+} for published analyses of Tasmanian waters is shown to vary widely at salinities up to about 1‰ , and to display a progressive reduction in variation up to about 11‰ ($\Sigma^{+} \approx 10^{5}$ /ueq. l^{-1}). At higher salinities, a low value is maintained with few exceptions. The accompanying figure illustrates this situation. The line defining the upper limit of the alkaline earth proportion between 1‰ and 11‰ salinity is proposed as a suitable demarcation between fresh and saline waters.

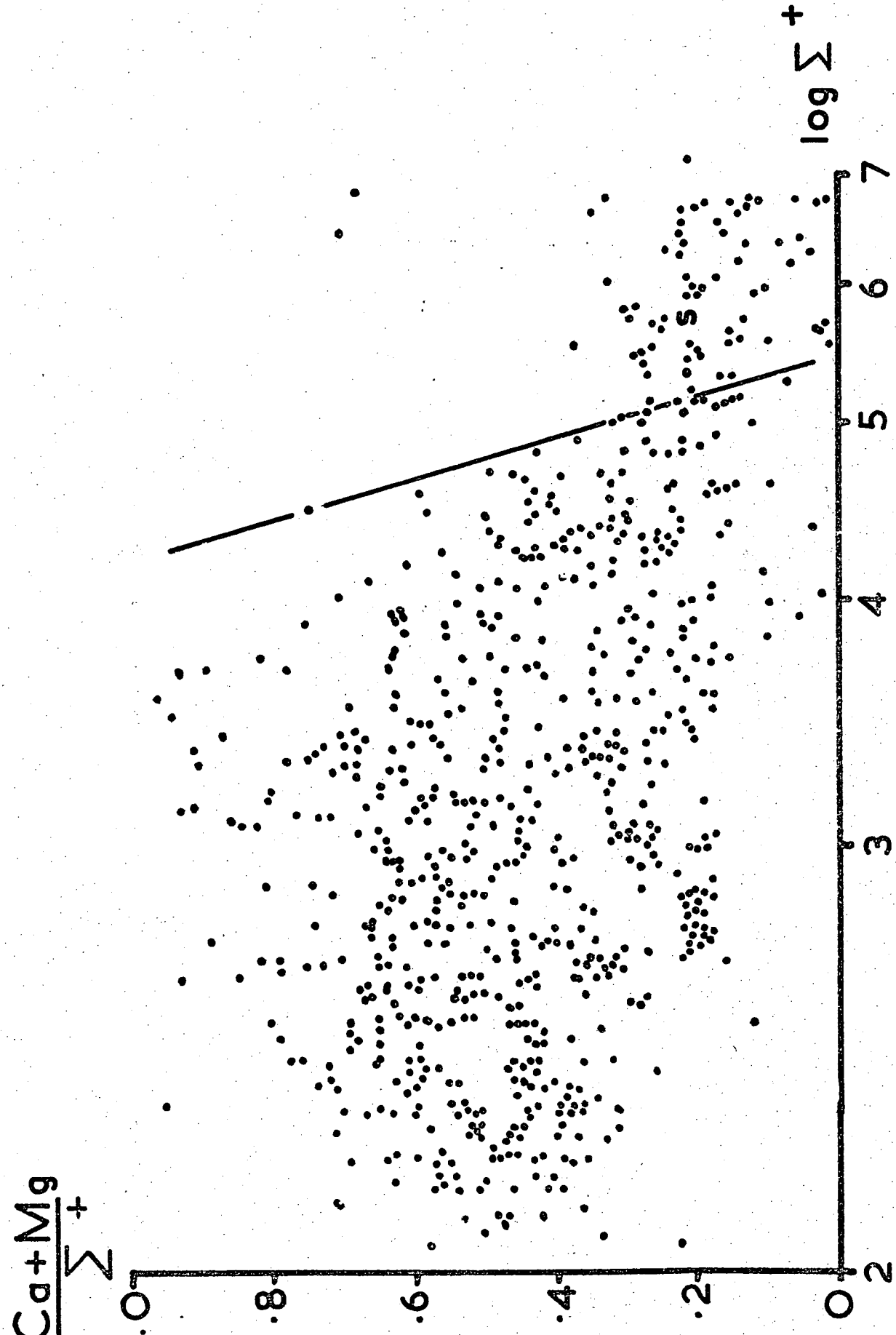
Thus, any water for which

$$\log \Sigma^{+} > 5.3 - 1.15 \frac{(Ca) + (Mg)}{\Sigma^{+}}$$ is called "saline".

This criterion defines saline waters as a discrete chemical class of waters with major ion composition limited by the solubility of alkaline earth salts.

APPENDIX FIGURE : THE VARIATION OF ALKALINE EARTH PROPORTION WITH TOTAL CONCENTRATION IN AUSTRALIAN WATERS.

S: SEAWATER


$\frac{Ca+Mg}{\Sigma^+}$
1.0
.8
.6
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.2
0
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$\log \Sigma^+$

CHEMISTRY OF SOME SEDGELAND WATERS: LAKE PEDDER, SOUTH-WEST TASMANIA

By R. T. BUCKNEY* and P. A. TYLER*

[Manuscript received 24 April 1973]

Abstract

Surface waters of the Lake Pedder area are characterized by low salinity, low pH, high colour, and a relative major-ion composition near that of seawater. Factors determining this composition are predominance of inert rocks, a covering of sedgeland peat isolating waters from rock contact, and a high rainfall brought by prevailing oceanic winds. Frequency and intensity of rainfall appear to determine the pattern of chemical variation. Salinity, bicarbonate, and pH may change rapidly during periods of high rainfall. Humic acids are important chemical constituents of the waters, and probably determine the type of biotic community which inhabits them.

I. INTRODUCTION

Lake Pedder lies at an elevation of 293 m in the valley of the Serpentine River, south-west Tasmania (Fig. 1). Landforms of the area are governed largely by the conformation of rocks of pre-Carboniferous age (Davies 1965) which are metamorphosed and largely resistant to chemical weathering. Prevailing winds are south-westerly, bringing high rainfall (Langford 1965) from the Indian Ocean. The mean annual precipitation at Strathgordon (3 years records' only) is 268 cm. The resistant nature of the rock and the high rainfall combined limit vegetation types to temperate rain forest or sedgeland (Jackson 1965), the latter being favoured in areas of low fertility, poor drainage or high fire frequency (Jackson 1968). Over most of the Pedder catchment a peaty sedgeland of *Gymnoschoenus sphaerocephalus* Hook. (Cyperaceae) and restio–epacrid communities overlie siliceous Precambrian rocks. Temperate rain forest occurs on south-facing flanks of surrounding hills.

The lake was formed by damming of the valley by glacial outwash from the Frankland Range (Davies 1965); the deposits have formed white or pink quartzite beaches around the lake, most extensively in the east where a dune and lagoon system has developed. Lake Pedder has a maximum depth of c. 3 m but considerable seasonal variation occurs and a wide expanse of beach is exposed in summer. With a maximum area of 9·7 km^2 it is the largest lake in the South-West. It is exposed and turbulent; summer temperatures range up to about 20°C (Bayly *et al.* 1966).

Apart from direct precipitation, the lake is fed by the upper reaches of the Serpentine River, which drains sedgeland. This extensive peat plain receives from flanking hills a number of creeks which become diffused in a maze of channels and seepages, which eventually coalesce to form the river which enters Lake Pedder through Lake Maria (Fig. 1).

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Several new or rare species of plants and animals have been discovered recently in the lake and the surrounding country (Bayly *et al.* 1972), and the area is the focal

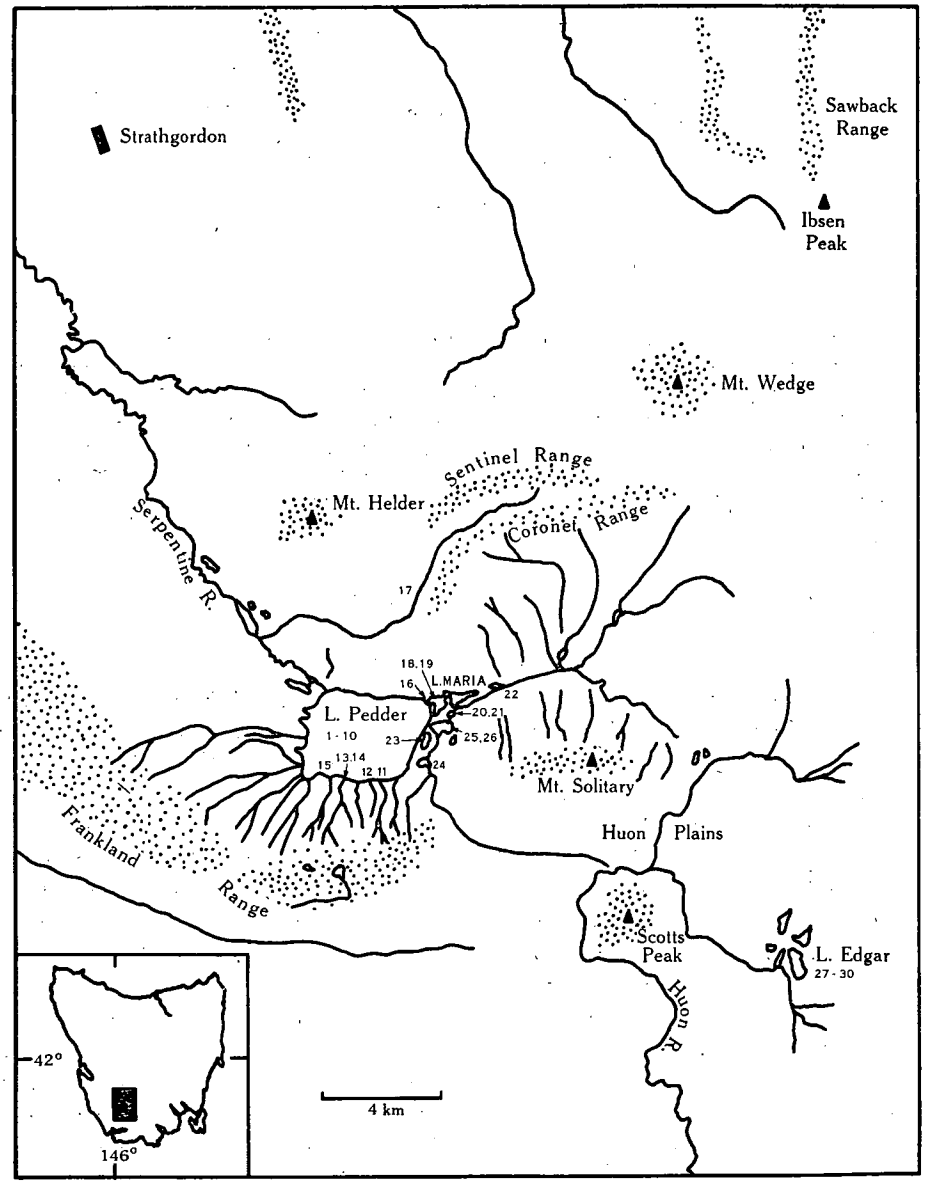

Fig. 1.—Map of Lake Pedder area showing sample sites. The numbers refer to samples in Tables 1 and 2.

point of controversy over plans for its inundation as part of a hydroelectric scheme nearing completion. Lake Edgar is a shallow lake on the peat plain east of Lake Pedder. It also will be inundated.

This paper outlines some chemical features of the aquatic biotopes.

TABLE 1

THE CHEMICAL COMPOSITION OF WATER IN LAKE PEDDER

+ indicates trace; — indicates undetectable

Sample	Date	TDS (p.p.m.)	TFS (p.p.m.)	K_{18} (μS/cm)	pH*	Colour (Pt units)	Na	K	Ca	Mg	Cl	HCO_3	SO_4	Fe	Mn	SiO_2	Turb. (J.T.U.)	OOF†
							←				μequiv./l.		→	←	p.p.m.	→		
1	6.iv.69	61·6	19·9	32·2	4·8	300	173	9	48	56	248	—	70	0·23	—	0·1		86·3
2	29.xi.69	38·1	17·7	35·4	4·8	120	140	8	52	61	200	15	37	0·12	—	0·2		87·9
3	13.ix.70	35·6	20·6	38·9	5·2	120	157	8	55	67	275	—	34	0·60	+		3·5	98·5
4	5.ii.71			39·6	5·62	120	152	13	60	74	254	42	38				1·6	84·2
5	23.ii.71			36·4	5·67	120	152	15	69	73	261	31	36				1·7	88·1
6	25.ii.71			36·7	5·72	120	176	21	71	75	289	35	30				1·5	90·4
7	5.iii.72			39·2	6·26	120	274	13	49	93	260	96	44	0·10	—		1·3	72·0
8	18.iii.72			51·4	4·64	150	387	15	56	166	451	12	60	0·28	—		1·7	95·5
9	3.iv.72			61·8	4·76	150					421	22	69				1·7	91·0
10	8.v.72			45·6	4·68	120	270	6	43	99	292	13	45	0·13	—		1·2	92·4

* Expanded-scale pH measurements made only after 5 February 1971.

† Oceanic origin factors after Anderson (1971).

TABLE 2

CHEMICAL COMPOSITION OF CREEKS AND LAGOONS NEAR LAKE PEDDER

+ indicates trace; — indicates absence

Sample	Location	Date	TDS (p.p.m.)	TFS (p.p.m.)	K_{18}*	Colour (Pt units)	pH†	Na	K	Ca	Mg	Cl	HCO_3	SO_4	Fe‡	Mn‡	Turb.§	OOF‖
								←				μequiv. $l.^{-1}$		→				
11	Creek 2	28.xi.69	31·4	14·0	40·3	100	4·5	129	8	26	44	211	—	19	—	—		101·6
12	Creek 3	25.ii.71			37·2	150	4·79	130	8	41	45	231	—	33			0·48	96·9
13	Creek 5	28.xi.69	37·8	13·8	34·9	120	4·8	121	5	24	74	220	—	23	0·05	—		100·2
14		25.ii.71			42·4	150	4·65	170	8	46	58	275	—	34			1·1	98·5
15	Creek 6	25.ii.71			33·1	150	4·90	137	13	52	57	228	—	33			0·5	96·7
16	Maria Creek	28.xi.69	50·4	17·8	39·8	150	4·9	154	10	45	74	287	—	48	0·12	—		94·8
17	Swampy Creek	26.ii.71			44·1	250	6·77	153	23	110	170	279	145	43				66·1
18	L. Maria No. 1	29.xi.69	54·1	21·0	41·9	200	4·8	152	13	60	83	324	—	35	0·46	—		99·9
19		24.ii.71			38·2	270	5·12	174	31	66	83	265	—	45			2·6	94·6
20	L. Maria No. 3	29.xi.69	32·5	17·1	36·5	60	5·2	133	6	33	49	251	9	12	+	—		102·2
21		24.ii.71			47·6	20	4·92	190	21	59	75	380	—	31			1·5	102·4
22	L. Maria No. 4	29.xi.69	63·0	21·2	22·2	200	4·8	167	11	47	85	234	36	69	0·32	—		76·4
23	L. Maria No. 5	29.xi.69	37·4	17·4	41·4	60	4·8	153	9	39	53	244	—	23	+	—		101·2
24	L. Maria No. 6	20.xi.69	51·2	20·2	58·3	80	4·8	189	9	33	69	271	—	27	0·05	—		100·7
25	L. Maria No. 7	29.xi.69	48·2	18·3	41·3	100	4·5	145	3	37	73	241	—	27	—	—		99·5
26		24.ii.71			35·8	220	5·01	163	15	66	73	208	—	42			1·27	92·1
27	L. Edgar	5.iii.72			46·1	100	6·37	294	20	79	136	301	151	51	0·11	—	2·0	66·2
28		30.iv.72			46·4	120	5·57	278	6	75	130	300	85	59	0·15	—	2·7	74·8
29		17.v.72			46·5	100	5·88	297	15	49	142	337	95	46			2·8	78·0
30		24.vi.72					5·67	266	15	40	128	289	78	46			2·0	77·5

* In μS/cm. † Expanded-scale pH measurements made only after 5 February 1971. ‡ In p.p.m. § J.T.U. ‖ Oceanic origin factors after Anderson (1971).

II. Methods

Samples were collected at irregular intervals in polyethylene bottles, and filtered through 0·5 μm pore-size membranes. Conductivity and pH were determined electrometrically. Bicarbonate was determined by titration of unfiltered water to an indicator end point of pH 4·5 (APHA 1965) or by automatic means, using a Radiometer PHM26pH meter and TTT11b automatic titrator coupled to an autoburette. Chloride concentrations were measured by conductometric titration (Golterman 1969) and sulphate determined by the ion-exchange procedure of Mackereth (1963). Analysis of metals was by atomic absorption methods using a Techtron AA5 instrument. Silicon was determined by the molybdate-yellow method (APHA 1965). Turbidity was measured with a Hach turbidimeter, and colour by visual comparison with glass disks in a Lovibond Nessleriser. Total Dissolved Solids (TDS) and Total Fixed Solids (TFS) were estimated by weighing the residues of a known volume of water after evaporation at 105°C and heating the residue at 600°C in platinum dishes. Dissolved oxygen was determined by the Winkler method, and temperature by a mercury thermometer or a thermistor.

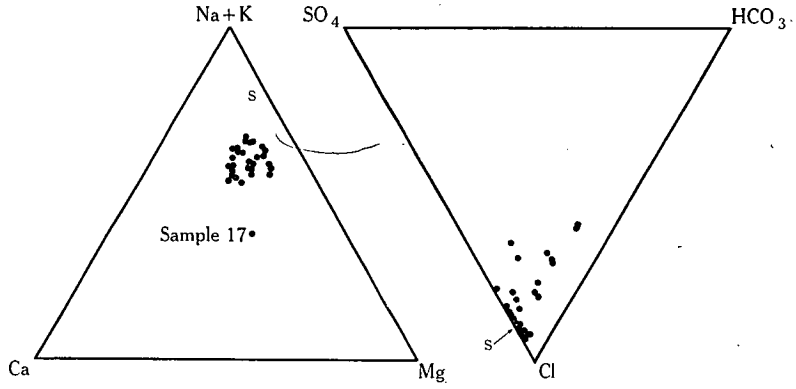

Fig. 2.—Ternary diagrams of ionic proportions of waters of the Lake Pedder area.
s: Relative proportions of ions in seawater.

III. Results

Analyses of Lake Pedder water samples are given in Table 1. Table 2 gives analyses of lagoons and lakelets in the Lake Maria complex, of Lake Edgar, and of creeks in the Pedder area. Ionic proportions are shown on the ternary diagrams (Fig. 2).

IV. Discussion

Lake Pedder is oxygen-saturated and homothermal, as expected of a shallow turbulent lake. The temperature was 15·4°C on 25 November 1969 and 24·0°C on 25 February 1971. The major chemical features of surface waters of the Lake Pedder area are their low ionic strength, high humic content, and a chemical composition similar to that of seawater. The last fact is obvious from the seawater order of ionic dominance ($Na > Mg > Ca > K$; $Cl > SO_4 > HCO_3$) of most samples, their high oceanic origin factors (Tables 1, 2) and the proximity of their plots on ternary diagrams to that of seawater (Fig. 2). There are occasional enrichments of magnesium, calcium, and bicarbonate (e.g. samples 4, 6, and 7 from Lake Pedder and samples 17, 27, 28, 29, 30 from adjacent areas — see Tables 1, 2) which disturb the usual seawater

dominance order. In the case of Pedder samples 4 and 6, since the bicarbonate and sulphate ions are present in near equal amount, the recorded change may reflect simply the relatively low precision of the sulphate method. In the third case, however, the change is real as it is accompanied by a marked increase in pH. The enrichments in Lake Edgar are probably attributable to the effects of a local dolomite outcrop. Apart from these enrichments of calcium, magnesium, and bicarbonate, many of these waters are very similar to the coastal lowland lakes described by Bayly (1964).

The general factors which operate to control major ion chemistry of waters in this area have been discussed by Buckney and Tyler (1973). Cardinal features are the predominance of old, inert rocks, a mantle of peat isolating waters from rock contact, and proximity to an ocean coast with strong prevailing winds bringing high rainfall. In such situations surface waters usually closely resemble seawater in relative composition (Tyler 1972), windborne sea spray being the major supplier of ions. In more general terms, the waters of the Lake Pedder area are similar to most of the brown, acid waters in the west of Tasmania (Buckney and Tyler 1973). The decomposition of sedgeland peats contributes considerable organic matter, accounting for high acidity, colour, and low bicarbonate content. Humic materials contribute greatly to TDS and conductivity, and the complexing ability of humic acids (Hingston 1963; Shapiro 1966) probably maintains the relatively high iron concentrations, though we have insufficient data to draw firm conclusions.

Normally, water levels in the lake are high from about late March and begin to fall around December. On the basis of qualitative observations of water heights on the dates listed in Table 1, there would seem to be evidence for a negative correlation between water height and pH, and a positive correlation between water height and ionic concentration, but this is probably complicated by rainfall intensity effects and the hydrological condition of the peat at any one time. Thus, heavy rain during 5–18 March 1972 — following a long dry period — resulted in a marked fall of pH (1·62 pH units) and a 50% rise in ionic concentration. This was followed by a slight decrease in ionic strength towards the winter months.

Results obtained during a dry period (February 1971) suggest that there was a sustained trend for both pH and ionic strength to rise. Seasonal changes in hydrological regime also affect ionic composition; with high lake levels, and considerable input of water from the creeks and Lake Maria, the oceanic origin factor remains high. After a long dry period, when lake levels are low and inflows greatly reduced, the oceanic origin factor falls and bicarbonate increases.

The meagre evidence from waters from the Lake Maria complex tends to confirm the above opinion. The Maria complex has lagoons which form part of the river flow-through system and also dune lagoons with poor drainage and no connection with the main systems. It is possible that the latter (e.g. sample nos. 20, 23) have somewhat different chemical regimes. In particular, they have a lower colour. Lagoon No. 4 (sample 22) may be anomalous since it appears to be part of the creek system but has a low oceanic origin factor.

The high acidity, intense colour, and low bicarbonate content probably preclude the establishment of sizable phytoplankton populations. It is more likely that bacteria utilizing allochthonous organic material form the basis of the food webs (Bayly *et al.* 1972).

V. Acknowledgment

Grateful acknowledgment is made of a grant (to P. A. Tyler) from the Australian Research Grants Committee.

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Stratification and Biogenic Meromixis in Tasmanian Reservoirs

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Abstract

Part of the Mersey–Forth hydro-electric scheme, Tasmania, Lakes Rowallan and Barrington are oligotrophic, slightly humic, warm monomictic reservoirs. Their flooded vegetation, shelter and deep V-section lead to pronounced clinograde oxygen profiles despite meagre autochthonous production.

With surprising rapidity, Lake Barrington developed a monomolimnetic pool which, when destroyed by severe floods, soon reformed. Though crenogenic and triptogenic elements may participate, principal causes of this partial meromixis are flooded vegetation and basin morphometry. The monimolimnion exhibits unusually large temperature rises and considerable enrichment of such chemical species as iron, manganese, hydrogen sulphide and bicarbonate. Iron is a major factor in the meromixis and largely accounts for marked monimolimnetic rises in electrical conductivity. The sharp upper monimolimnetic boundary is an almost horizontal chemocline, above which the mixolimnion behaves as a warm monomictic lake. Winter ventilation of its hypolimnion is tardy but complete. The monimolimnion is therefore maintained by decomposition and basin morphometry, not climate.

Attendant chemical phenomena of prolonged anoxia in hypolimnetic or monimolimnetic water pose alleviable problems when that water is used domestically, industrially or for power generation.

Introduction

Present demands for freshwater lead to construction of many reservoirs, often sited in precipitous valleys of large rivers offering suitable dam sites, ready water supplies, large storage volumes, or high heads of water for power generation.

Such reservoirs usually stratify and are morphometrically predisposed to hypolimnetic anoxia. In this reducing milieu, iron, manganese and hydrogen sulphide readily dissolve, often with undesirable consequences. In extreme cases, biogenic meromixis ensues.

In two new Tasmanian reservoirs anoxic hypolimnia developed. In one, a monimolimnetic pool developed with surprising rapidity.

Materials and Methods

Temperature and dissolved oxygen were determined electrometrically (Mackereth 1964). Occasionally the Alsterberg–Winkler test (American Public Health Association 1965) was used. Transparency was measured with a Secchi disk and water telescope.

From water samples taken with 5-litre Van Dorn samplers, temperature, E_h, pH and conductivity (K_t) were immediately measured electrometrically on board in flow-through cells preventing atmospheric contact (Fig. 1). Redox potentials from oxygenated strata were converted to E_7 values (Hutchinson 1957). Conductivity

was corrected to 18°C. Total sulphides were titrated iodometrically (Golterman 1969) in aliquots of unfiltered samples treated with zinc acetate and sodium hydroxide (American Public Health Association 1965). Alkalinity and sulphate were determined on unfiltered water, soon after sampling, by titration to pH 4·5 (Mackereth 1963) and by ion exchange with conductometric measurement (Mackereth 1955) respectively.

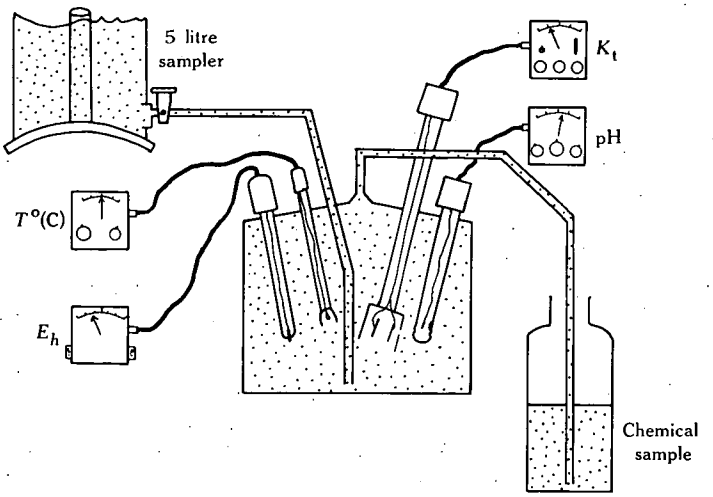

Fig. 1. Diagram of a flow-through cell for electrometric measurements of anoxic samples. A sample for chemical analysis, which can be kept anoxic by sealing, is taken simultaneously.

Iron and manganese were determined as follows. From January to April 1970 untreated samples were returned to the laboratory. In transit iron precipitated. Samples were homogenized and membrane-filtered, and iron and manganese then determined in acidified filtrates (A), and precipitates redissolved in hydrochloric acid (B). The sum A + B was taken as the soluble iron originally present. After May iron and manganese were determined by atomic absorption spectroscopy of unfiltered samples acidified in the field to pH *c.* 1·0 (C). Samples determined as before showed that C practically equalled A + B and samples membrane filtered and acidified in the field (D).

Other analyses were of water filtered through 0·5 μm membranes several days after collection. Total Dissolved Solids (TDS) and Total Fixed Solids (TFS) were determined by evaporation followed by 1 hour's incineration at 550°C. Derived from stored samples, hypolimnetic values may be underestimates because of iron precipitation. Colour was measured with a BDH Nessleriser. Chloride was determined conductometrically (Golterman 1969). Cations were measured by atomic absorption spectroscopy. Density was determined gravimetrically; samples from anoxic strata were maintained anoxic at low temperature until weighed.

Descriptive Background

The Mersey and Forth Rivers flow northwards from Tasmania's Central Plateau, draining extensive uplands of dolerite. In steep-sided gorges of midreaches dams have been constructed, forming deep narrow reservoirs. Fig. 2 shows main features

of the hydro-electric scheme and new reservoirs. Our attention was centred on Lakes Rowallan and Barrington.

Lake Rowallan flooded extensive marshy plains and forest in the Mersey Valley (Fig. 3). The dam, *c.* 42·5 m high, produces full storage water levels 490 m above mean sea level. Sides slope steeply near the dam but gently in upper reaches (Figs. 3, 5). Water drawn from the base of the dam operates hydro-electric turbines.

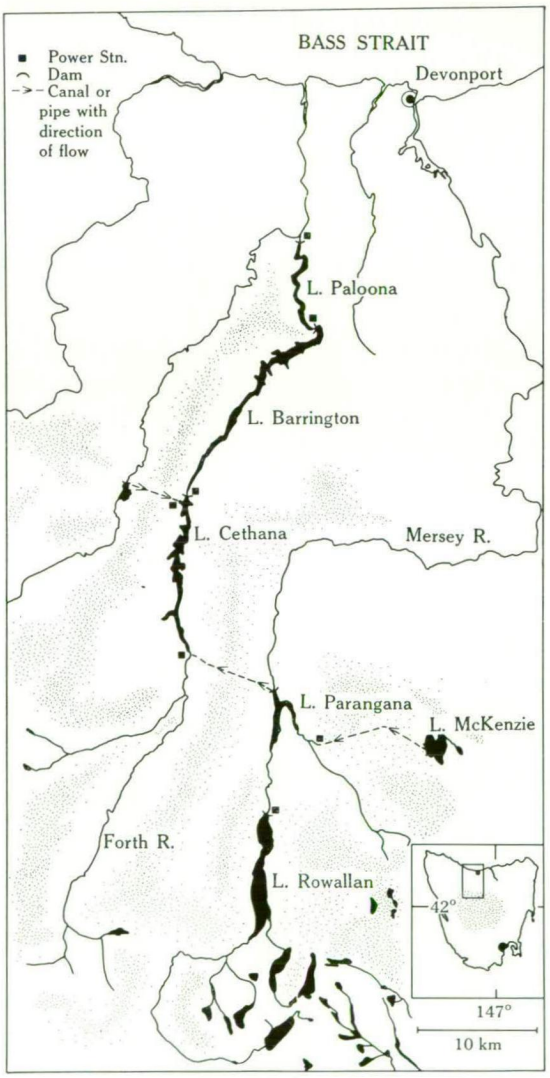

Fig. 2. Sketch map showing main features of the Mersey–Forth hydro-electric scheme, Tasmania.

Devils Gate Dam, *c.* 76 m in height, impounded water in the steep-sided Forth Valley, forming Lake Barrington (Figs 4, 6). Water for turbines is withdrawn to 17 m below full storage height of 122 m above mean sea level. The lake flooded dense forest but a narrow band of felling prevented trees projecting from the lake over the operating range of levels. Both the Mersey and Forth Rivers drain sclerophyll forests, *Restio*-epacrid heathland and temperate rain forest, and contain allochthonous colour.

Results

Morphometry

Bathymetric maps and derived morphometic parameters are shown in Figs 5 and 6 and Table 1 respectively.

Surface Water Chemistry

The few 'global' parameters (Dussart 1967) presented in Table 2 characterize the waters as soft and slightly acid, with some humic materials. Barrington is slightly more saline and has higher colour. Prevailing ionic dominance orders are $Ca > Mg > Na > K : HCO_3 > Cl > SO_4$ or $Na > Ca > Mg > K : Cl > HCO_3 > SO_4$ as is usual for this area (Buckney and Tyler 1973).

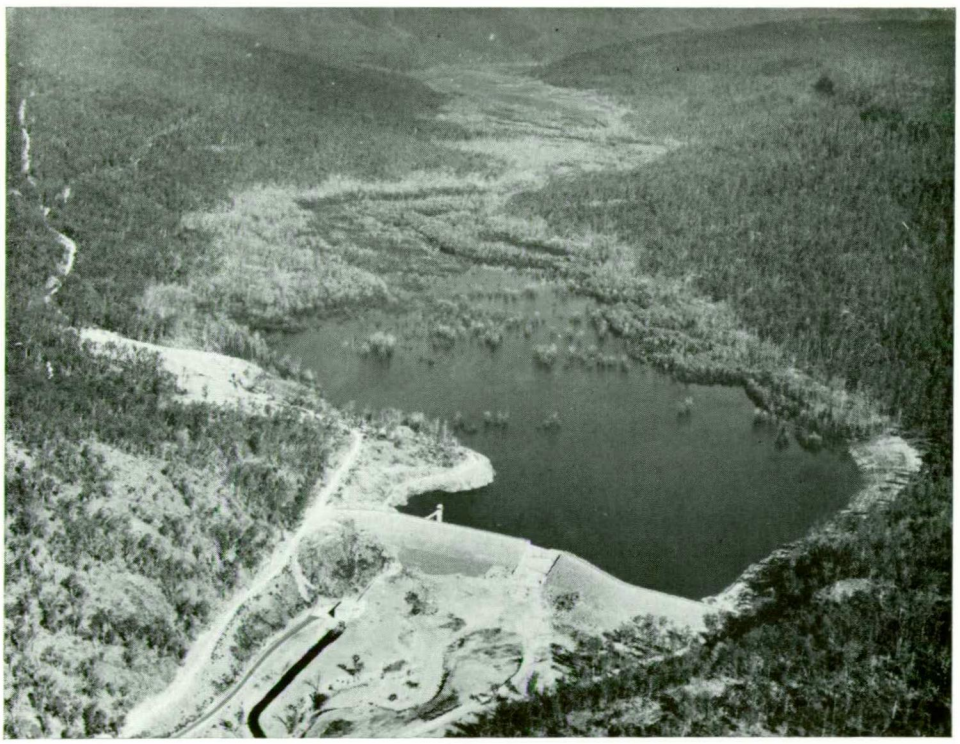

Fig. 3. Lake Rowallan from the South, at a low water level. The light areas show the extent of vegetation flooded at high water level.

Stratification—Temperature and Oxygen

Rowallan's seasonal regimes of temperature and oxygen are shown in Fig. 7. Extensive draw-down after 1970 removed the hypolimnion and influenced shapes of oxygen and temperature curves. Previously, the bottom 7 m of hypolimnion were anoxic, and comparison with Barrington (Fig. 8) and other Tasmanian reservoirs (Tyler 1974) indicates that, if undisturbed, the whole hypolimnion would become anoxic.

Data for Barrington are shown in Fig. 8. When investigations began the lowest strata were anoxic, with marked temperature rise. Subsequently, as metalimnetic temperature gradient increased, hypolimnetic oxygen concentrations declined, though complete anoxia was still restricted to bottom layers where temperatures rose.

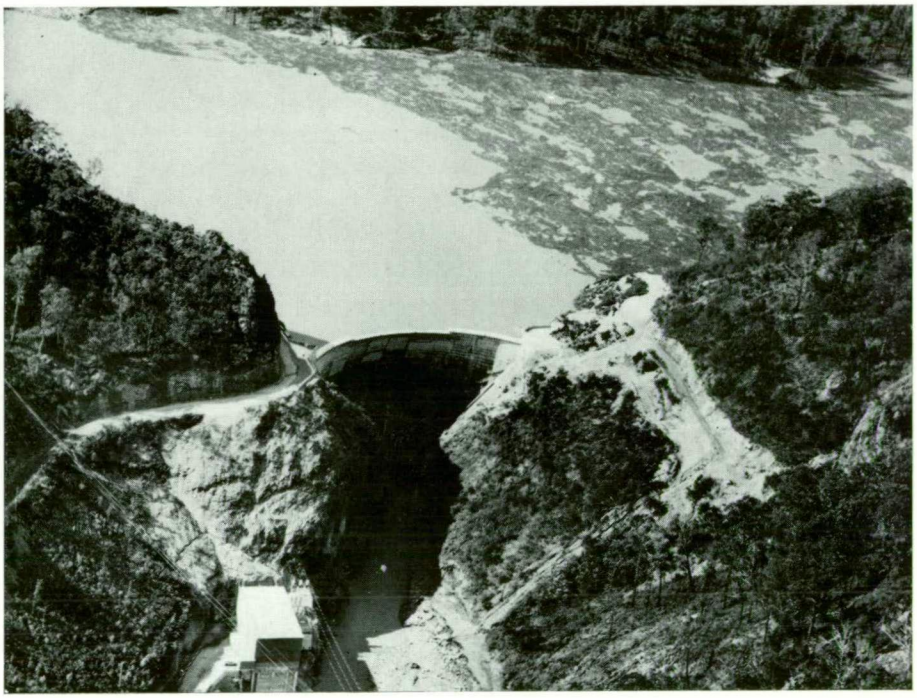

Fig. 4. Devils Gate Dam and Lake Barrington from the East. The logs brought down by the floods of August 1970 were later removed.

Table 1. Morphometric parameters of Lakes Rowallan and Barrington

Parameter	Rowallan	Barrington
Area	8·9 km²	7·8 km²
Length	10·7 km	18·8 km
Width	1·6 km	1·9 km
Mean width	0·8 km	0·4 km
Max. depth	*c.* 35 m	*c.* 72 m
Mean depth	15·5 m	27·1 m
Max. volume	*c.* 0·13 km³	*c.* 0·23 km³
Length of shoreline	28·2 km	52·3 km
Shoreline development	3·8	5·3

Pronounced hypolimnetic oxygen bulges of March intensified in April, coalesced in May, and just persisted in June when prominent oscillation developed in the residual metalimnion. Meanwhile anoxia increased upwards beyond the zone of bottom heating, and by June the bottom 40 m were anoxic except for remnant bulges.

By July the lake was practically isothermal at about 6°C, except for the zone of bottom heating. The lake was oxygen-saturated down to about 30 m where oxygen

fell to about 70% of satuation. Where bottom heating commenced, oxygen concentrations declined dramatically to zero. This discrete bottom layer appeared to be monimolimnetic.

Devastating floods swept down the Mersey–Forth valleys in August, and water rose 3 m above the crest of Devils Gate Dam. The lake was turbid with flood-borne silt, and temperature and oxygen profiles undulated complexly. Temperatures increased gently from top to bottom without the previous increase over a discrete

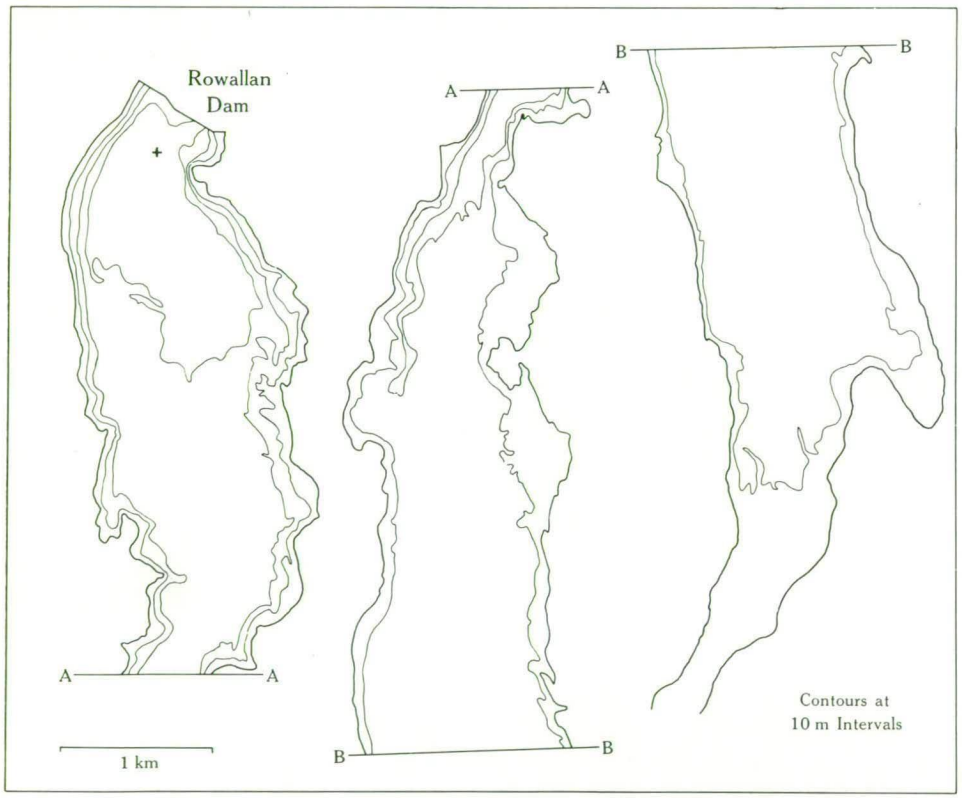

Fig. 5. Bathymetric map of Lake Rowallan, simplified from a pre-impoundment map. The cross indicates the sampling site.

Table 2. Global chemical characteristics of surface waters of Lake Rowallan and Lake Barrington

Reservoir	Dates	Colour (hazen)	TDS (ppm)	TFS (ppm)	Major ions (m-equiv. l^{-1})	K_{18} (μS cm^{-1})	pH
Rowallan	Apr. 68–Feb. 70	5–10	12·4–25·6	14·1–17·8	0·414–0·512	23·0–27·3	6·1–6·5
Barrington	Dec. 69–Aug. 70	10–40	25·0–35·2	13·6–21·8	0·438–0·659	24·2–33·0	6·2–7·2

stratum of bottom water. Nine months later, on 18 May 1971, pre-flood conditions had been restored. The thermocline was eroding and ventilation of the hypolimnion had begun. The zone of anoxia still coincided with a sensible rise in temperature over a discrete bottom stratum.

Two years later, on 16 September 1973, similar conditions prevailed, with slight diminution in oxygen across a remnant metalimnion and a dramatic fall to anoxia precisely where temperature rise began in the bottom 3 m of water (Fig. 8).

Fig. 6. Bathymetric map of Lake Barrington based on a pre-impoundment map, Lands and Surveys Department. The cross represents the sampling site and the stippled area the approximate extent of the monimolimnion determined by interpolation of isobaths and by temperature–oxygen measurements in September 1973. Contours at 15 m intervals.

Chemical Effects of Stratification

Both reservoirs showed classical effects of stratification—profound changes in chemistry of anoxic hypolimnia. In Lake Rowallan iron and manganese increased to 3·61 and 1·10 mg/l respectively by February 1970, and hydrogen sulphide was liberated from turbine effluents. Iron was precipitated in the river bed.

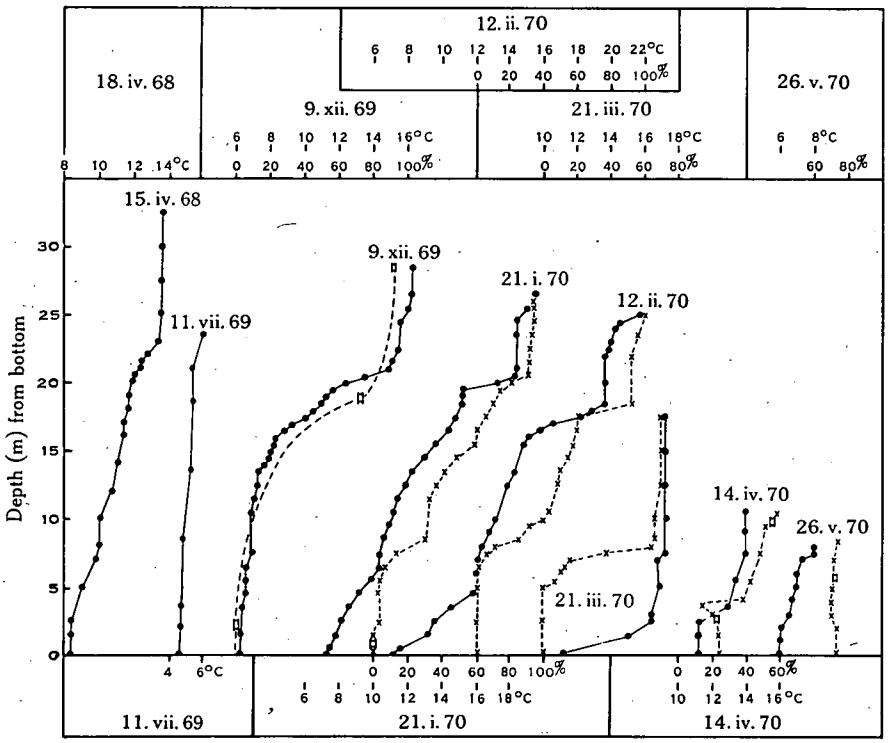

Fig. 7. Temperature (●) and dissolved oxygen (×) profiles for Lake Rowallan. Open rectangle, Winkler test.

In Lake Barrington large increases in TDS, K_{18} and various chemical species marked the level of anoxic water. Lowered redox potentials indicated the reducing nature of this monimolimnetic water (Fig. 9), which stank of hydrogen sulphide. In June 1970, when the anoxic zone extended upwards almost to the remnant thermocline, gaseous hydrogen sulphide reaching the surface (Fig. 9) could be smelled from the banks.

Changes in concentration of major cations and anions with depth are shown in Fig. 10. Again, sudden increases in concentration coincided with the bottom temperature increase.

Monimolimnetic water from Lake Barrington was green-black and smelled of hydrogen sulphide. A sample brought to the surface was immediately transferred anoxically to a flow-through cell, sealed, and warmed to 18°C. The relationship between conductivity and temperature remained strictly linear. Bubbling air through the sample then produced rapid colour change from green-black to golden, a concomitant rise in conductivity (Fig. 11), and evolution of hydrogen sulphide. As

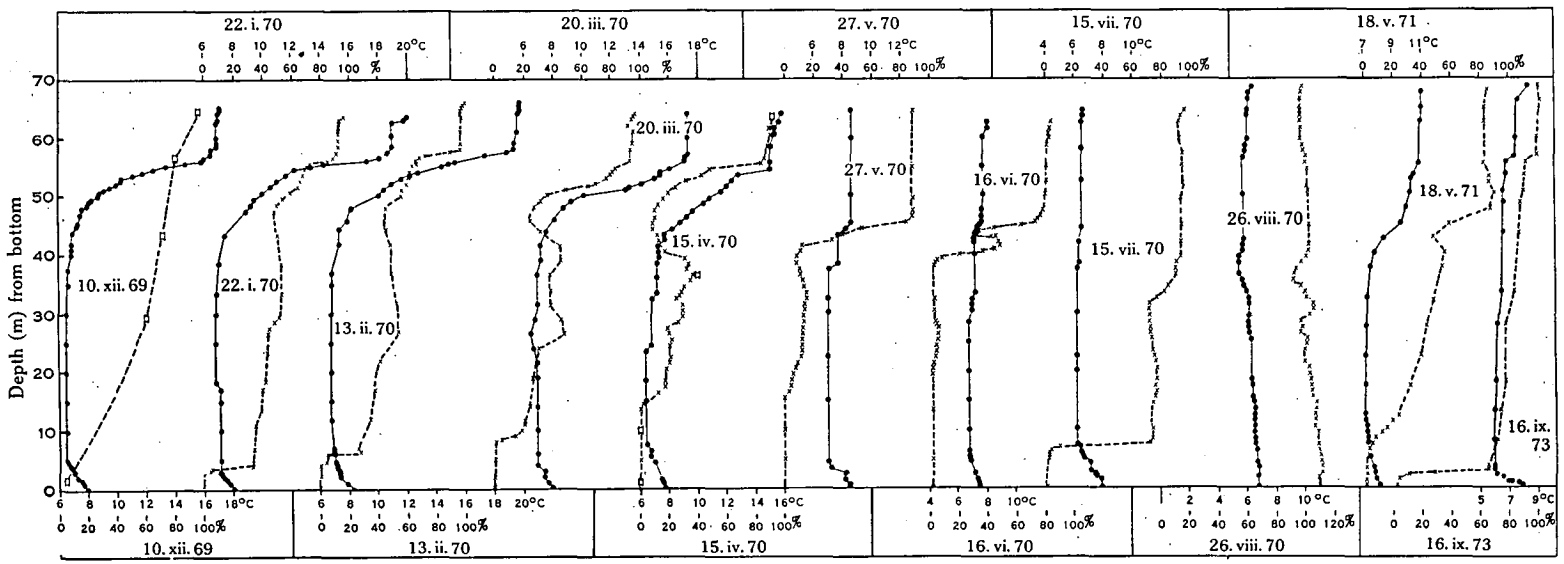

Fig. 8. Temperature (●) and dissolved oxygen (×) (meter) profiles for Lake Barrington. Open rectangle, Winkler test.

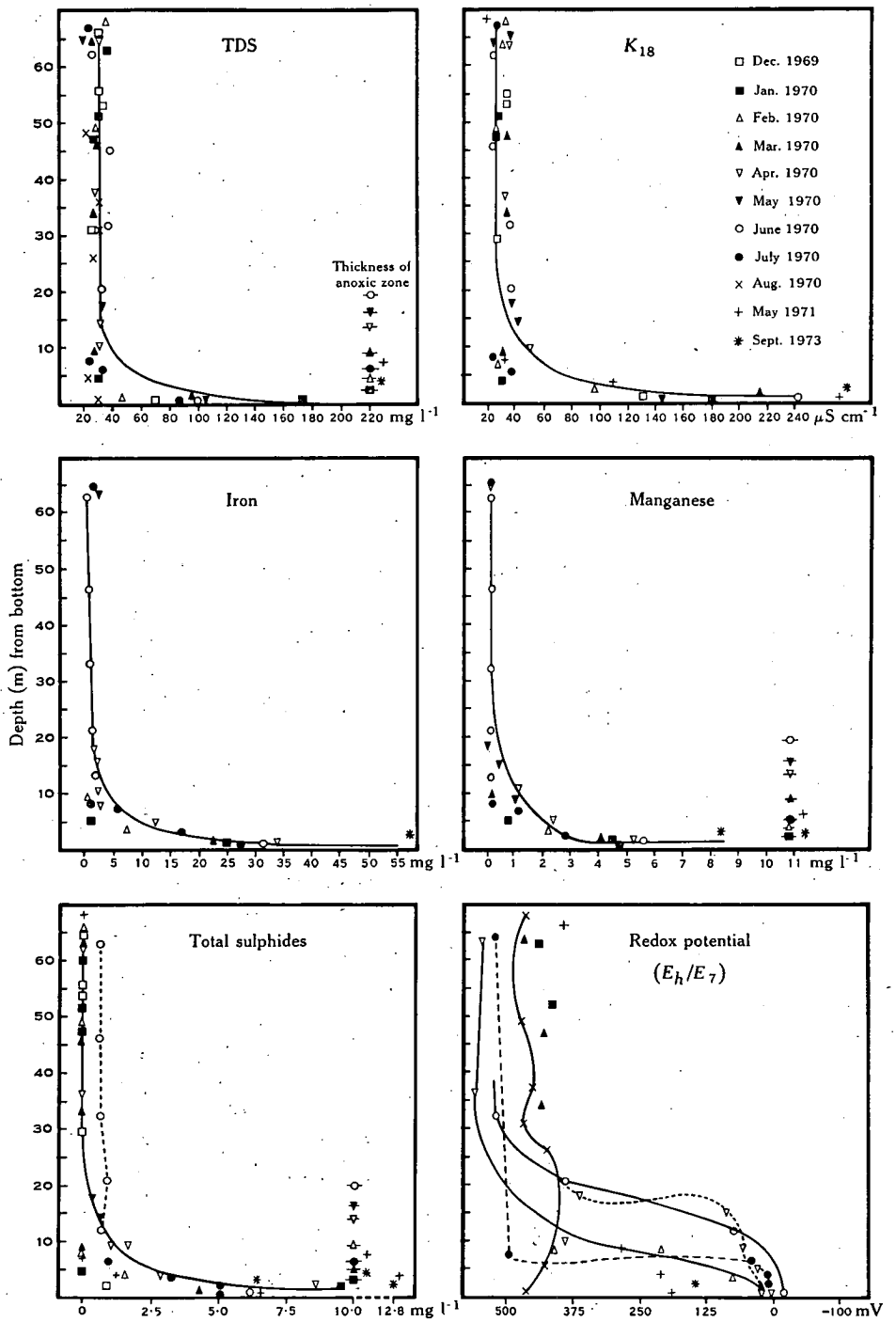

Fig. 9. Profiles of various chemical properties in Lake Barrington from 1969–1973. Redox potentials in the oxic zone are corrected to pH 7·0. Except in the case of E_7 values, continuous lines are drawn through the maximum values obtained, irrespective of sampling date. The points lying below the line represent stages in the development and erosion of the maximum chemical effects of stratification as the thickness of the anoxic zone above the monimolimnion increased or decreased to zero.

aeration continued conductivity fell steadily to a minimum, while a flocculent brown precipitate, presumably iron hydroxide, developed.

A sealed sample was aerated in the laboratory several days later. Transition to the golden stage had taken place during transit, and there was no initial rise in conductivity, but a fall to a minimum as the flocculent precipitate formed (Fig. 11).

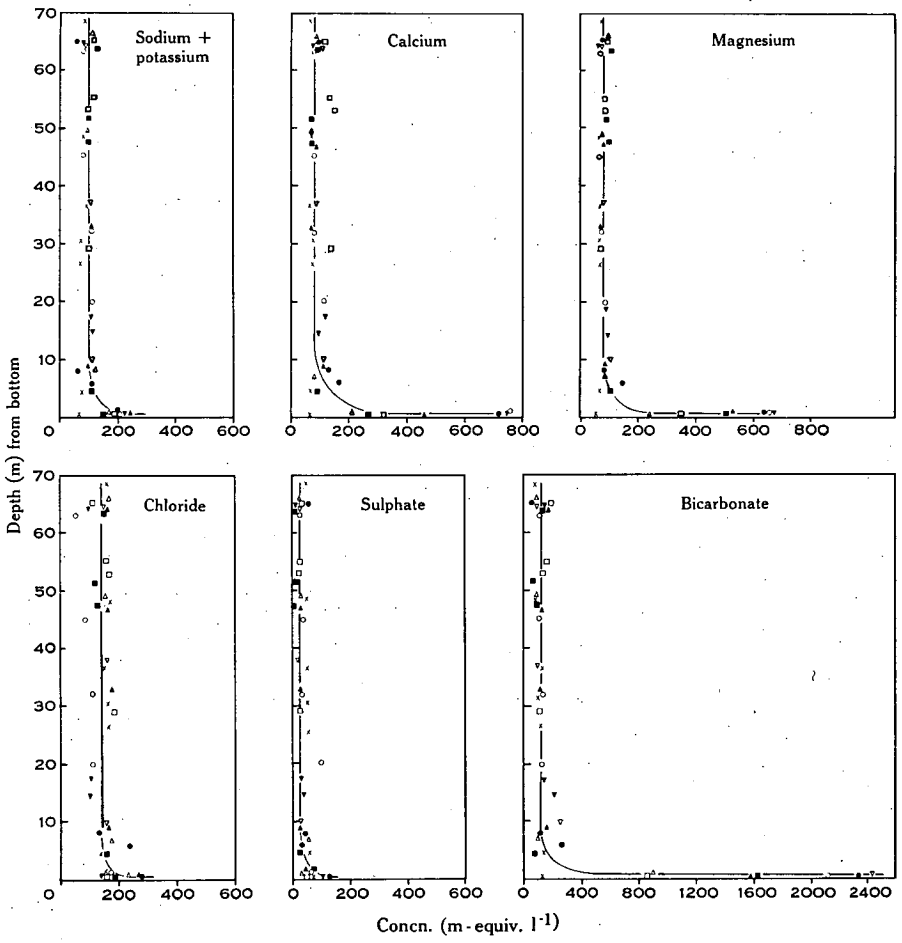

Fig. 10. Profiles of major cations and anions in Lake Barrington from 1967 to 1973. Other details as for Fig. 9.

There was considerable difference in density between epilimnetic and monimolimnetic water—0·9983 and 0·9989 g cm^{-3} respectively at 20°C. The value for monimolimnetic water after aeration and removal of the precipitate was 0·9984 g cm^{-3}.

Discussion

The reservoirs studied show familiar seasonal cycles of stratification and holomixis. They are warm monomictic (Hutchinson and Löffler 1956), or cheimomictic (Bayly and Williams 1973), like most lakes and reservoirs in Tasmania which stratify (Tyler 1974). Their waters are soft, and ionic dominance orders show considerable geochemical influence (Buckney and Tyler 1973).

In terms of temperature gradient and attendant chemical phenomena, stratification is most severe in Lake Barrington. Low hypolimnetic oxygen concentrations remain for considerable periods with only a remnant of thermal stratification (e.g. June–July 1970), as expected in deep reservoirs of narrow profile.

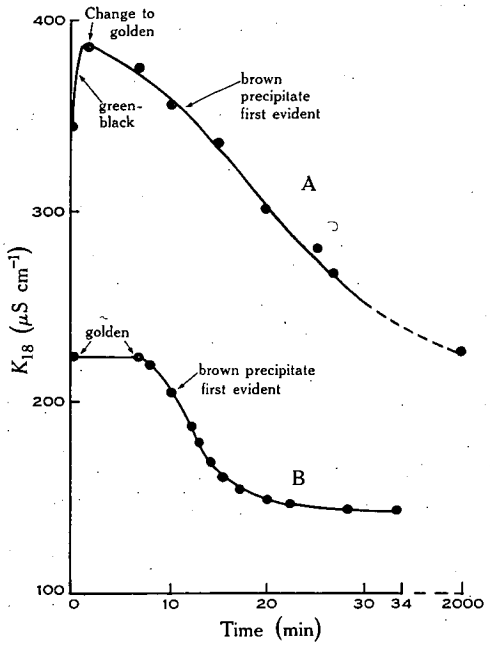

Fig. 11. Changes in K_{18} on aeration of anoxic water from the monimolimnion of Lake Barrington, September 1973. Sample A was brought to the surface, sealed in a flow-through bottle on ice, then warmed to 18°C and aerated a few minutes after sampling in a mobile laboratory on the lake shore. Sample B was kept sealed on ice for 3 days before aeration commenced. The total iron concentration of sample B was 55 mg l^{-1}.

The coincidence of sudden oxygen depletion and temperature rise near the bottom suggests a monimolimnetic pool in the deepest part, a view strengthened by sharp increases in dissolved substances in this region (Figs 9 and 10). This being so, the progressive development of anoxia above the monimolimnion (Fig. 8) is unconnected with events in the stratum beneath, and the mixolimnion is a stratified lake in its own right (see also Kjensmo (1967), p. 253; Meriläinen (1970), p. 35). Since monimolimnetic features are limited to the bottom 6–8 m water column, and hence extend only a short distance upstream of the dam, it is appropriate to regard Lake Barrington as warm monomictic with a monimolimnetic pool rather than as a meromictic reservoir.

Devils Gate Dam was closed in July 1969 and by November Lake Barrington was almost full. Such rapid filling is expected, since its volume is only 10% of average annual flow, but equally rapid development of a monimolimnetic pool is surprising and raises the question of its genesis. It seems that at least two, and probably three, mechanisms have contributed.

First, decomposition of dense, flooded vegetation produces hypolimnetic anoxia. High oxygen demands are usual in new reservoirs even without flooded vegetation (Lyman 1944). The deep V-section of the reservoir predisposes it for biogenic meromixis. Even low trophogenic production can produce heavy oxygen demand in the small volume of deep tropholytic strata. This is sufficient to produce biogenic meromixis through accumulation of iron, the primary factor in biogenic meromixis (Kjensmo 1962, 1967, 1968*a*; Meriläinen 1970). The concentration of iron in the

pool of Lake Barrington is less than in some natural meromictic lakes, where values may exceed 300 mg/l iron. Nonetheless there is considerable build up, and a conductivity gradient of 200 μS cm^{-1}, which is present in Lake Barrington, imparts high meromictic stability to Lake Svinsjøen (Kjensmo 1968*b*). As well as for iron, monimolimnetic enrichment of calcium, magnesium, manganese and bicarbonate adds to stability.

In biogenic meromixis no enrichment of sodium and chloride usually occurs in the monimolimnion, but is expected in crenogenic meromixis (Yoshimura 1937) resulting from influx of saline spring water. Slight enrichment of these ions in Lake Barrington (Fig. 10) suggests an element of crenogenesis, as in Valkaijärvi (Meriläinen 1970). However, since calcium, magnesium, and especially iron, increase to a much greater extent, it is likely that biogenic factors are much more significant.

The rapidity with which the pool developed suggests that a third mechanism, triptogenesis, lent a hand. Perhaps silt laden water, from major construction work progressing at Cethana while Barrington filled, entered the reservoir as a density current, triggering biogenic meromixis as early agriculture did for some Austrian lakes (Frey 1955). Density currents appear to be regular phenomena of deep narrow reservoirs with large inflows, and are detected as turbidity currents, dissolved oxygen minima (Wiebe 1939, 1940) or dissolved oxygen maxima (Lyman 1944). In Lake Barrington density currents produced dissolved oxygen bulges between 15 m and 40 m from the bottom (Fig. 8). In the August 1970 floods they bore great quantities of silt. Whatever the early causes, the pool probably accumulated by down-slope migration of water with a density increased by dissolution of materials in the anoxic hypolimnion.

That the floods destroyed the monimolimnetic pool raises the question of its permanence. The degree of chemical enrichment is sufficient to maintain meromixis in many natural lakes, though they do not have the massive inflows of Lake Barrington. However, the flood was severe, and by May 1971 the monimolimnetic pool was reestablished (Fig. 8). At the very least, Lake Barrington is a case of partial meromixis, the period of stagnation depending on sporadic variation in local conditions (Findenegg 1937). It is likely to persist until swept out by occasional floods, the thickness of the monilimnetic pool meanwhile increasing as down-slope migration continues.

Meromictic lakes are typical of continental climates where late ice melts followed by rapid heating prevents full hypolimnetic ventilation (Strøm 1945; Hutchinson 1957; Kjensmo 1968*b*). In Tasmania, where dimictic lakes do not occur (Tyler 1974), meromixis of Lake Barrington depends instead on abundant organic matter of flooded vegetation, and on the form of the sheltered basin (cf. Northcote and Hasley 1969). Other reservoirs now being constructed or planned in Tasmania are likely to have similar conditions. At present, however, the only other record of meromixis in Australia is of a highly saline lake in Victoria (Timms 1972).

The monimolimnetic temperature rise of Barrington cannot be explained fully. The maximum gradient (September 1973) of 1·9°C is more than usually reported. Lake Barrington is also unusual in the thinness of the chemocline over which this increase takes place. Hutchinson (1957) and Meriläinen (1970) conclude that combined effects of geothermal heating and exothermic reactions cannot explain much smaller temperature rises than those in Barrington. Though radiation heating may occur in shallow meromictic lakes such as Skjennungen (Kjensmo 1967), this

hardly applies to Barrington, even allowing for down-slope migration. One possibility is that heat was transported by warmer density currents.

Meriläinen (1970) presumes that iron and manganese are major causes of monimolimnetic increase in conductivity, and Kjensmo (1967) considers Fe^{2+} the dominating cation in the high electrolyte content of monimolimnetic waters. The data of Fig. 11 demonstrate the involvement of iron. In sample A, aerated very shortly after sampling, the initial rise in K_{18} is attributed to a change from Fe^{2+} to Fe^{3+}, as redox potentials rise. Since potentials rise rapidly once minute amounts of oxygen are present (Hutchinson 1957), this would occur before precipitation of iron, which requires oxygen. Traces of oxygen must have reached Sample B during the 3 day transit; it was golden in colour when aeration commenced. On taking the conductance of 1 m-equiv. l^{-1} Fe^{2+} at 18°C as 44 μS cm^{-1}, the removal of 55 mg l^{-1} Fe by precipitation should cause a fall in K_{18} of 43 μS cm^{-1}. The observed fall was 86 μS cm^{-1} (Fig. 11), so that 50% of the observed change could be attributed to iron. Further indication of the major contribution of iron is given by the fact that after precipitation and removal of iron, the density of monimolimnetic water is almost equal to that of the epilimnion.

Chemical events associated with thermal stratification pose problems for water supply and power generation, especially when hypolimnetic water is drawn off. When oxygenated in passing through turbines it releases hydrogen sulphide, which corrodes metal, paint and equipment. In the Mersey Valley hydrogen sulphide could be smelled for several kilometres below Lake Rowallan. The problem can be acute in tropical countries (Douglas, in Lowe-McConnell (1966), p. 50; Begg 1970). Also, iron is oxidized and blankets the rocks. At low flows, the Mersey River has appeared as a rusty streak for several kilometres below Lake Rowallan.

Perhaps the most nagging problem with anoxic hypolimnetic water is that of manganese. In solution or as insoluble oxides it interferes with industrial processes and domestic supplies, and it may also be precipitated by bacteria on pipeline walls, with many undesirable consequences (Tyler and Marshall 1967*a*, 1967*b*). Such problems are widespread in Australia and overseas (Tyler 1970). To overcome these problems such techniques as turbine or tailrace aeration (Wisniewski 1965) or artificial hypolimnion aeration (Fast 1968; Speece 1971) have been developed.

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Chemistry of Tasmanian Inland Waters

Abstract

A few of Tasmania's several thousand lakes and rivers have been sampled in a preliminary survey of water chemistry. They range in concentration from extremely dilute glacial lakes (TDS < 10 ppm) to hypersaline lagoons (TDS > 85‰), the majority being dilute (TDS < 50 ppm). The 3 mechanisms controlling water chemistry proposed by Gibbs (1970) are seen to operate and the 3 terminal water types showing precipitation-dominance, rock-dominance and solubility-limited composition are found, together with a range of intermediates. The majority of waters have seawater ionic composition or moderate geochemical modification of this.

Contents

1. Introduction

Most of Tasmania's several thousand lakes have never been investigated chemically or biologically. The only previous survey is that of Williams (1964, 1967) though scattered information on various waters is contained in the publications of Bayly et al. (1966), Nicholls (1958), Powell (1945) and Weatherley (1958).

This survey aimed to investigate the chemical nature of as many Tasmanian waters as possible. In this paper we have divided Tasmania into 5 Provinces based partly on climatic or geological criteria but mainly on topographic or arbitrary grounds. The latter was unavoidable for areas of complex geology or sparse information and such Provinces contain a mosaic of different water types. Nonetheless, some are real water chemistry provinces where distinctive water types predominate over large areas, determined by predominance of one environmental factor.

2. Methods

Water samples were collected in polyethylene bottles and stored at 4 °C for 1–6 weeks before analysis. Colour was measured with a comparator and pH and conductivity (K_{18}) electrometrically. Bicarbonate was determined titrimetrically on unfiltered samples (American Public Health Association, 1965). All other analyses were of water filtered through 0.45 μ membranes. Chloride was determined by conductometric titration (Golterman, 1969), sulphate by the method of Mackereth (1955) and silica by the molybdate yellow method (American Public Health Association, 1965). Cations were determined by atomic absorption spectroscopy. Total Dissolved Solids (TDS) and Total Fixed Solids (TFS) were determined by evaporation in platinum dishes followed by ignition at 600 °C.

3. General Descriptive Background

Tasmania lies within latitudes affected by the westerly air stream of the Roaring Forties. This fact, and the disposition of mountain ranges, accounts for the west-east rainfall gradient (Fig. 1). Mean July temperatures range from 0 °C–10 °C while

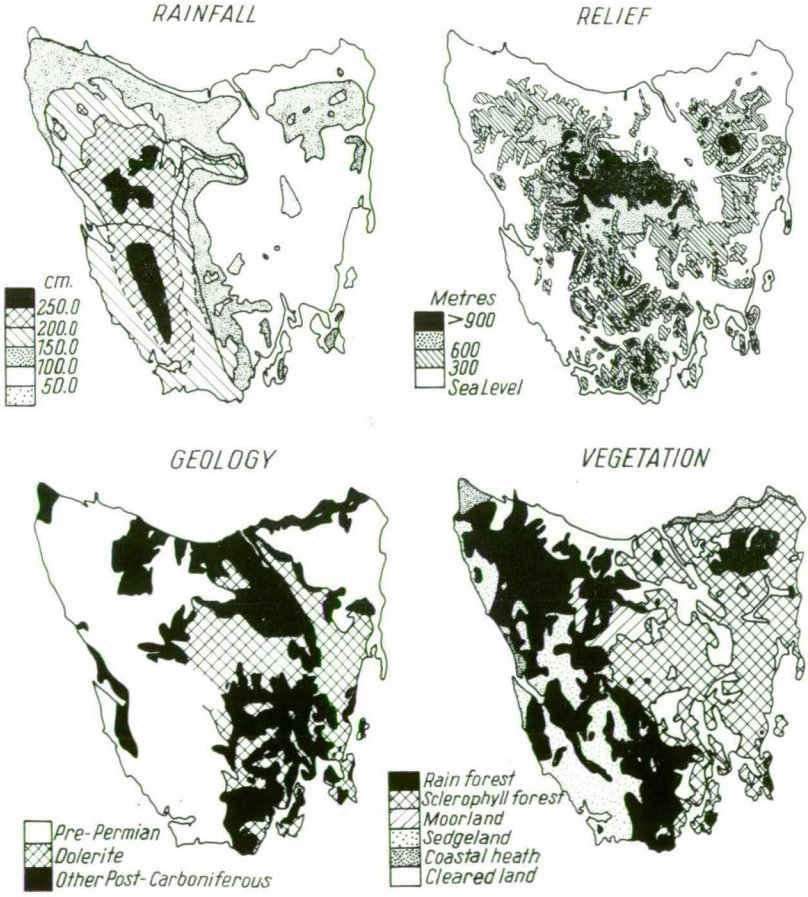

Fig. 1. The general pattern of relief, rainfall, geology and vegetation of Tasmania. Simplified from several authors in Davies (1965)

those for January vary from 10 °C–18 °C. More than half the island lies at an elevation greater than 300 m, the only extensive lowland plains occuring in northern coastal and Midland areas (Fig. 1). There is a major geological discontinuity from west to east, the metamorphosed pre-Permian rocks of the western regions contrasting with the Central Plateau and drier eastern areas which are dominated by Jurassic dolerite (Fig. 1). This climatic and geological discontinuity is reflected in pronounced vegetational differences, temperate rain-forest or sedgeland dominating the wet areas while dry sclerophyll or epacrid heath covers the drier East (Fig. 1).

Most of the several thousand lakes lie within the areas occupied by Pleistocene ice sheets or cirque glaciers (DERBYSHIRE et al., 1965). The large shallow lakes of the eastern Central Plateau were subject to periglacial activity.

The climate, geomorphology, geology and vegetation of Tasmania have been treated in detail by the authors BANKS, DAVIES, JACKSON and LANGFORD in DAVIES (1965), and by JACKSON (1968) and SPRY and BANKS (1962).

In a general way Tasmania can be divided into 5 water chemistry provinces reflecting these prevailing environmental features. Inevitably, there is some overlap but such a division seems to represent broad differences and at the same time facilitates discussion of a large amount of data.

4. Results

a) Province I – the South-West and West

Analyses of samples from lotic and lentic localities shown in Fig. 2 are given in Table 1.

The South-West waters vary in composition depending on the nature and degree of geological influences. At the one end of the spectrum are brown, acid waters (Samples 1–15a, 28–32) with the sea water order of cationic and anionic dominance i. e. $Na > Mg > Ca > K$: $Cl > SO_4 > HCO_3$. Ionic proportions of these are near those of seawater (Fig. 3). At the other end of the spectrum are the waters showing the marked geochemical influence of weatherable rocks not covered by deep peats. Samples 33 and 34 drain the serpentenite of the Sawback Range and are magnesium-calcium-bicarbonate dominated. Samples 35–37 are influenced by the dolomite on the northern flanks of the Mt. Anne massif. Between these extremes are diverse waters showing various degrees of geochemical influence. Square Lake (Sample 14) and Hanging Lake (Sample 13) are high altitude lakes on the pre-Cambrian quartizites of the Arthur Range. Geochemical influence is minimal and they resemble the acid, seawater type except that humic influences are absent. We expect many cirque lakes in the metamorphosed fold ranges of the South-West to be of this type. Samples 25–27 are high altitude waters of uncertain status from the geologically-complex Mt. La Perouse. Samples 18–24 taken from lakes on the dolerite of Mt. Picton and Mt. Field show slight geochemical modification of atmospheric supply and resemble closely the dolerite waters of the Central Plateau (Province II) while Nos. 38–54, all rivers, show various influences which need further investigation.

The geology of the West Coast area is complex and sedgeland peats are replaced generally by yellow podzolic soils (NICOLLS and DIMMOCK, 1965). Only 4 lakes were sampled. Lake Rolleston (Sample 15) (Tyndall Range) and Lake Bellinger (Sample 15a) (coastal dunes) both have near-seawater ionic proportions. On Frenchman's Cap, Lake Vera (Sample 16) shows only slight geochemical influence but Lake Tahune is calcium-magnesium-bicarbonate dominated. Only one lotic water retains the seawater dominance order, the others showing various degrees of calcium and bicarbonate additions.

Table 1. Chemical characteristics of surface waters of the South-West and West of Tasmania. The sample numbers refer to the locations indicated in Fig. 2. + indicates a trace, – indicates undetectable

Location	No.	TDS ppm	TFS ppm	K_{18} $\mu S \cdot cm^{-1}$	pH	Colour Pt units	Na^+	K^+	Ca^{++}	Mg^{++}	Cl^-	HCO^-_3	SO_4^{--}	SiO_2 ppm	Fe ppm
							←			μeq/l			→		
Quartz Drainage, Port Davey	1	65.2	30.0	70.8	4.5	140	304	17	42	103	472	0	27		+
Peat Bog, P. Davey	2	67.2	26.0	66.1	4.5	160	283	15	60	100	460	0	32	–	–
Mine Pool, P. Davey	3	56.2	24.2	59.0	4.9	100	266	23	42	93	420	0	80		0.20
Peat Pool, Blakes Opening	4	76.0	6.0	53.0	4.2	280	239	24	13	23	315	0	33	0.2	–
Lake Pedder	5	38.1	17.7	35.4	4.8	120	140	8	52	61	200	15	37	0.2	0.12
Lake Maria 1	6	54.1	21.0	41.9	4.8	200	152	13	60	83	324	0	35	–	0.46
Lake Maria 3	7	32.5	17.1	36.5	5.2	60	133	6	33	49	251	9	12	–	+
Lake Maria 4	8	63.0	21.2	22.2	4.8	200	167	11	47	85	234	36	69	–	0.32
Lake Maria 5	9	37.4	17.4	41.4	4.8	60	153	9	39	53	244	0	23	–	+
Lake Maria 6	10	51.2	20.2	58.3	4.8	80	189	9	33	69	271	0	27	–	0.05
Lake Maria 7	11	48.2	18.3	41.3	4.5	100	145	3	37	73	241	0	27	–	+
Peat seepage, Strathgordon	12	35.2	17.4	32.4	4.7	100	118	21	35	58	248	0	21	–	0.09
Hanging Lake	13	21.8	13.6	25.1	6.0	< 5	104	12	35	42	86	16	30	0.7	–
Square Lake (Arthur Ra.)	14			28.6	5.6	30	103	8	28	36	181	5	26		
Lake Rolleston	15			27.3	5.1	50	98	10	39	45	181	3	28		
Lake Bellinger	15a	80.4	46.2	99.5	5.6	100	683	34	67	197	727	35	76		
Lake Vera	16	38.4	17.6	28.8	7.0	70	122	13	85	101	150	96	11	0.2	–
Lake Tahune	17	26.8	12.8	26.3	6.8	30	78	8	100	92	114	120	13	–	–
North Lake	18	34.8	21.4	28.9	7.3	10	126	15	55	50	169	51	11	2.0	–
Lake Picton	19	18.3	9.0	31.0	6.8	< 5	94	8	27	56	175	14	53	2.0	–
Lake Riveaux	20	24.8	17.0	30.2	7.2	< 5	100	13	95	67	148	95	8	3.1	–
Lake Dobson	21	27.6	18.1	31.7	6.5	< 5	57	5	135	100	126	205	8	6.8	–
James Tarn	22	17.4	5.8	14.0	6.9	< 5	74	14	55	38	90	70	20	2.7	–
Lake Seal	23	23.8	14.0	21.6	7.2	< 5	70	3	80	58	147	105			–
Lake Webster	24	24.6	12.6	22.4	7.2	15	87	3	75	58	153	85			–
Ouse Lake	25			36.8	6.7	15	187	20	43	65	295	22			0.14
Tarn, Leaning Tree Saddle	26			34.4	6.4	70	163	18	30	38	210	160			–
Pigsty Ponds	27			34.6	6.5	50	183	19	33	53	250	118			–
Melaleuca Ck., P. Davey	28	62.4	23.0	71.8	4.3	140	313	19	42	103	472	0	27		+
Louisa River	29	71.8	29.8	67.4	5.3	160	287	37	74	145	495	0	44		0.34
Ck. 2 L. Pedder,	30	31.4	14.0	40.3	4.5	100	129	8	26	44	211	0	19	0.3	–
Ck. 5, L. Pedder	31	37.8	13.8	34.9	4.8	120	121	5	24	74	220	0	23	0.3	0.05
Honeymoon Ck. –, L. Pedder	32	50.4	17.8	39.8	4.9	150	154	10	45	74	287	0	48	–	–
Ck. on Sawback Range	33	41.6	30.8	63.0	7.7	< 5	135	16	95	325	190	338	56		–
Adam River	34	109.2	92.2	167.9	7.6	60	183	16	1255	708	300	1610	17	2.1	0.30
Weld River	35	211.0	148.2	309.2	7.7	40	187	302	2000	2055	450	3620	22	2.8	–
Sandfly Ck.	36	142.4	88.6	214.5	7.9	20	152	14	1550	1250	255	2170	16	2.6	–
Little Florentine River	37	152.2	121.4	245.6	7.8	15	135	14	1760	1558	199	2480	16	5.9	–
Huon River	38	64.1	28.1	57.8	7.0	120	183	17	206	180	255	271	37	2.5	0.12

Picton River	39	53.4	31.0	46.5	7.1	60	170	12	215	133	249	269	39	4.1	+
Styx River	40	92.2	68.4	148.7	7.7	15	252	28	450	709	410	1200*	39		–
Savage River	41	71.2	64.8	125.4	7.1	50	326	28	240	500	516	583*	160	4.2	0.15
Farm Ck.	42	53.4	29.2	46.1	6.5	5	192	31	75	104	342	31	29	4.2	0.30
Bulgobac Creek	43	41.8	24.2	39.6	6.2	50	157	23	65	92	256	22	31	4.2	0.20
Fossey River	44	34.2	24.2	39.3	5.6	20	144	23	53	101	200	110	13	4.5	–
Hatfield River	45	33.2	22.6	38.2	6.8	50	122	10	70	104	231	129	10	25.0	0.10
Waratah Creek	46	29.2	29.6	40.5	7.4	< 5	139	20	185	98	245	102	16	3.5	–
Que River	47	35.6	21.2	36.3	6.8	30	135	18	65	104	254	67	25	3.1	0.35
Magnet Ck. Res'r	48	32.2	21.0	40.5	6.5	15	152	19	65	185	275	60	23	3.1	–
Henty River	49	37.8	19.6	39.8	7.4	50	148	15	95	94	266	74	23	1.9	–
Mackintosh River	50	36.6	19.6	36.0	7.5	70	100	20	130	61	163	170	19	1.8	0.10
Yollande River	51	28.2	16.6	32.4	6.2	50	122	15	45	73	230	33	23	1.0	0.25
Murchison River	52	32.6	14.8	21.1	7.5	50	78	13	45	37	174	33	20	2.0	0.10
Whyte River	53	57.4	30.4	58.0	6.8	40	187	8	110	221	249	231	51		0.20
King River	54	29.8	16.4	34.3	6.4	30	96	13	90	65	175	89	32	1.6	–

* Bicarbonate concentration reduced for further calculations

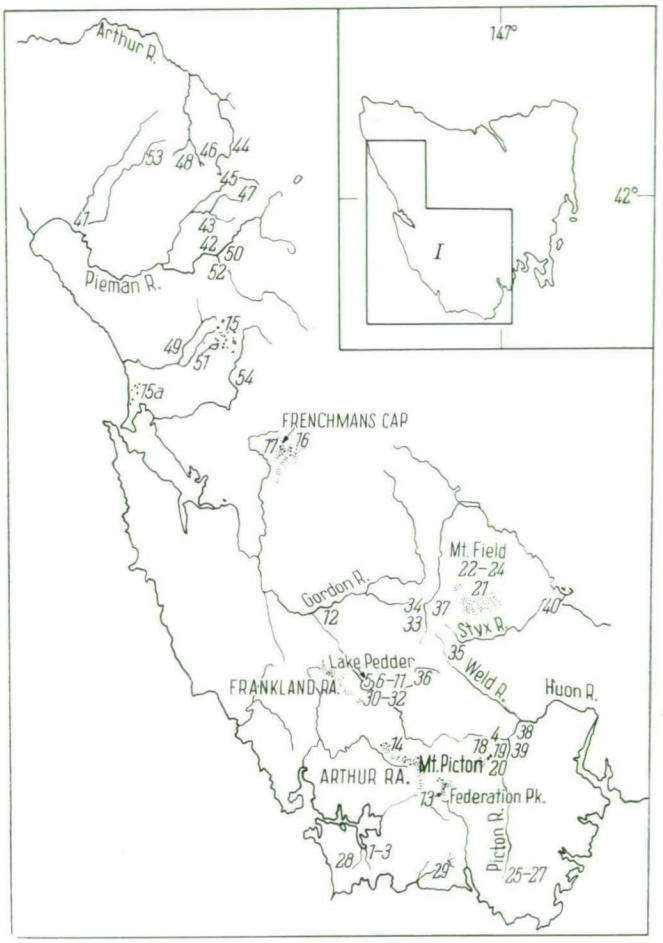

Fig. 2. The location of sample sites in Province I–the South-West and West of Tasmania. Numbers refer to the samples in Table 1

b) Province II – The Central Plateau

The Central Plateau is an area of dolerite > 600 m in altitude. About 5,000 small lakes of glacial origin lie on the western side, with rainfalls > 100 cm, and on the eastern side, where rainfalls are less, there are several large, shallow lakes (Fig. 4). Results of analyses are shown in Table 2. The high rainfall lakes, including Arthurs Lake and Great Lake, are very dilute (TDS < 20 ppm) with seawater order of ionic dominance prevailing. However ionic proportions are displaced away from seawater (Fig. 5) and Ca and HCO_3 tend to become second dominants, particularly in the larger lakes on the east of the Plateau where higher mean temperature and lower rainfall also result in higher ionic concentrations.

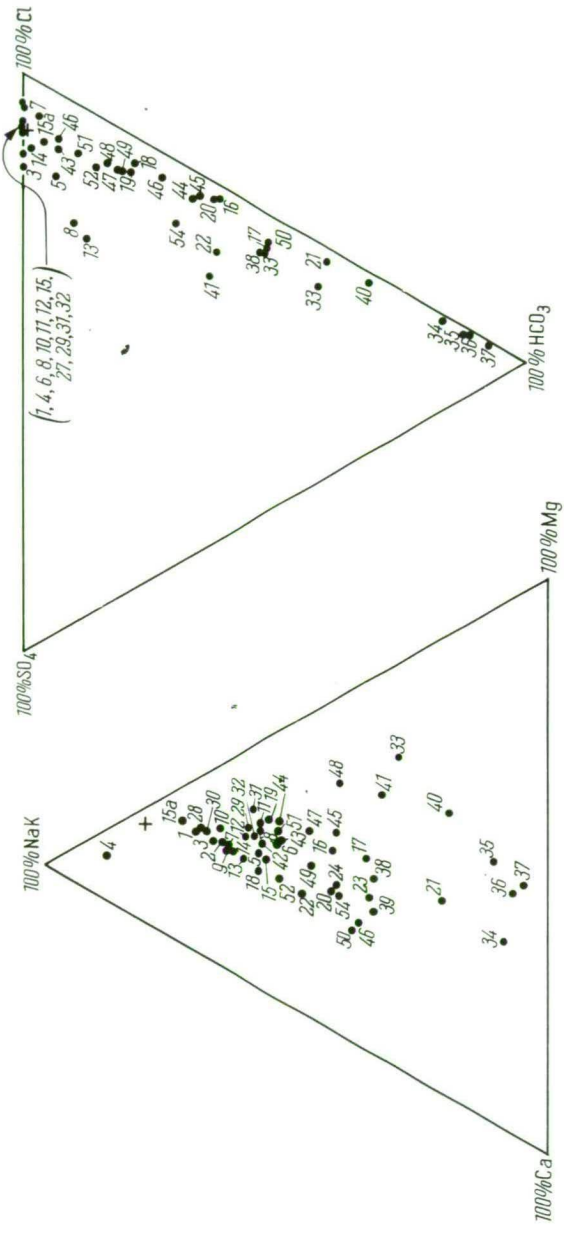

Fig. 3. Ternary diagrams showing ionic proportions of waters from Province I–the South-West and West of Tasmania. The numbers refer to sample numbers in Table 1.
+ indicates seawater proportions.

Included in this category are the large lakes Woods, Sorell and Crescent. The high ionic concentration of Lagoon of Islands is a special case brought about by heavy transpiration losses from a floating mat of reeds and islands which covers the basin.

Most Central Plateau waters are colourless but in the west local sedgeland may contribute allochthonous humic material (Samples 1,4). Brownwater Lagoon (Sample 38), near Lake Crescent, is a shallow swamp, the authochthonous brown colour deriving from decaying Angiosperms. Concentrations of iron in Central Plateau waters are low but, sporadically, Lake Sorell has shown high concentrations (Sample 36).

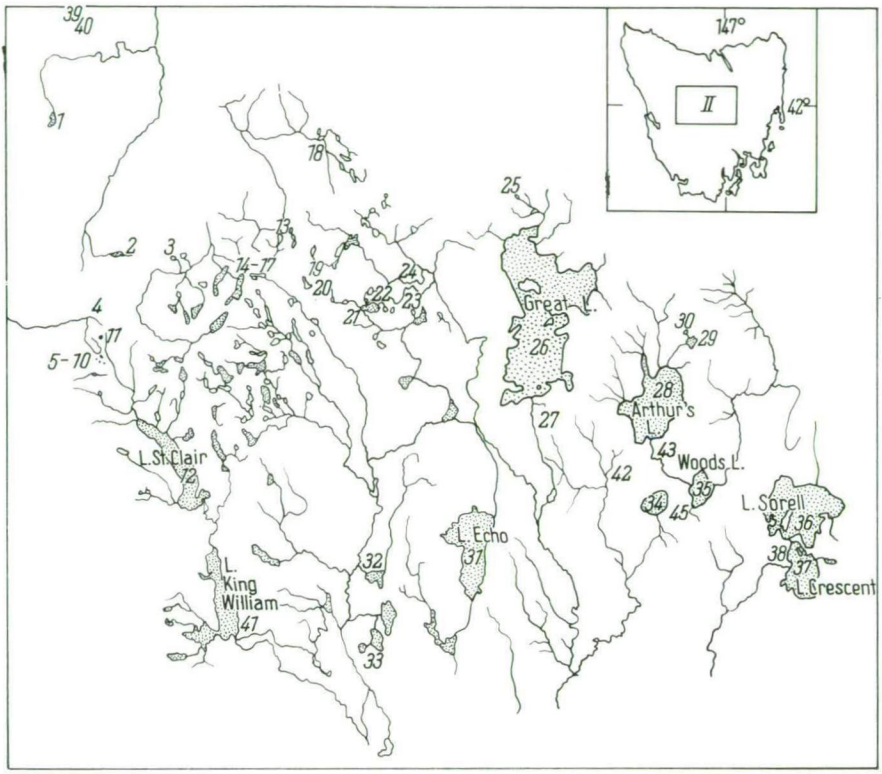

Fig. 4. The location of sample sites in Province II—The Central Plateau of Tasmania.

c) Province III — The North-West

The geology of the North-West is complex and a wide variety of waters is found. The majority sampled (Fig. 6) have the dominance order $Na > Mg > Ca > K$: $HCO_3 > Cl > SO_4$ (Table 3). The anionic order suggests geochemical contribution but there are considerable ion imbalances which may be attributed to over-estimation of bicarbonate in the solid phase (GOLTERMAN, 1969). If bicarbonate is calculated as $HCO_3 = \Sigma^+ - (SO_4 + Cl)$ then the $Cl > HCO_3 > SO_4$ order is restored.

A few lotic samples show considerable enrichment by calcium or magnesium bicarbonate (Samples 8–13). Maracoopa Creek drains limestone caves and limestone also outcrops in the Mersey catchment. Magnesium dominance in some creeks may be derived from Tertiary olivine basalts.

Waters draining coastal heaths (Samples 5,21) resemble the brown waters of the South-West in dominance order but are more concentrated. Humic coastal waters of this type also occur on the Bass Strait Islands and the North East.

It seems likely that atmospheric ions form the main supply in this area except where readily-soluble rocks are exposed.

d) Province IV — The Midlands, East and North

Most of the eastern part of Tasmania is dry (mean annual rainfall < 75 cm), especially in the far North-East and Midlands where evaporation may exceed precipitation and closed lakes occur. There are many shallow lagoons in this Province (Fig. 7),

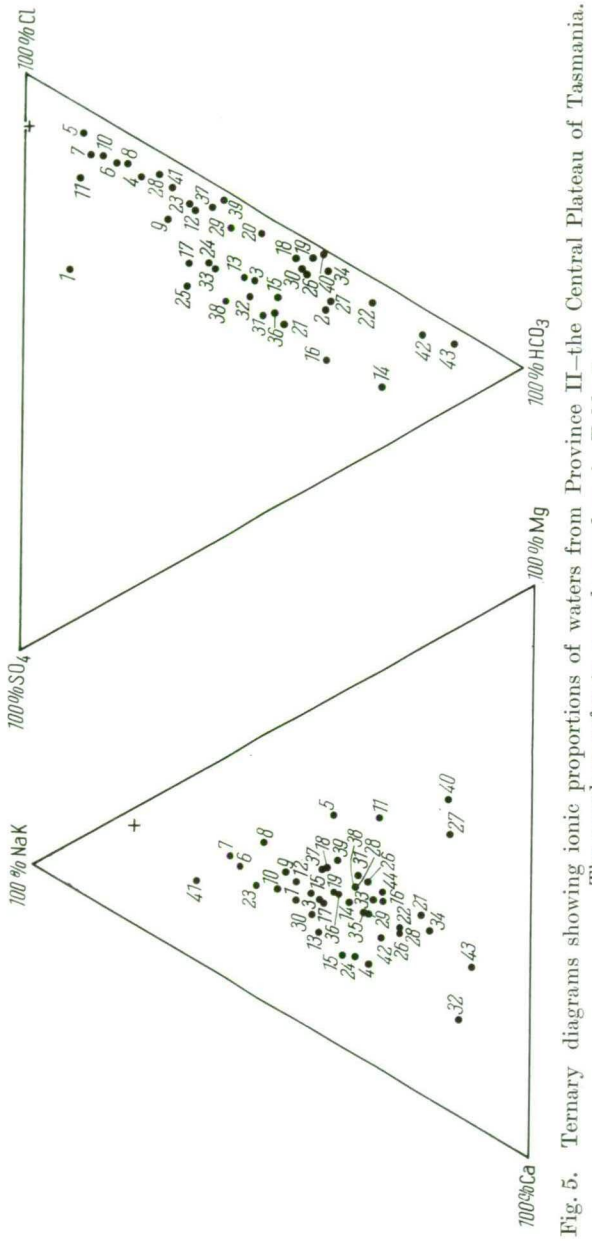

Fig. 5. Ternary diagrams showing ionic proportions of waters from Province II–the Central Plateau of Tasmania. The numbers refer to sample numbers in Table 2.
+ indicates seawater proportions.

most of which have not been sampled. The ones sampled (Table 4) were saline (Samples 1–6) as recorded by Williams (1964). The Tunbridge Lagoons (Samples 3,4) appeared to be closed lakes and were highly saline. Sodium chloride dominance was usual but Tunbridge No. 4 was magnesium chloride dominated. The coastal lagoons of the North-East have seawater-type composition but they differ from the South-West waters and Bass Strait Islands lagoons in having low colour, high pH, relatively high calcium and high salinity. Many of the eastern rivers had the excess bicarbonate phenomenon noted in the North-West.

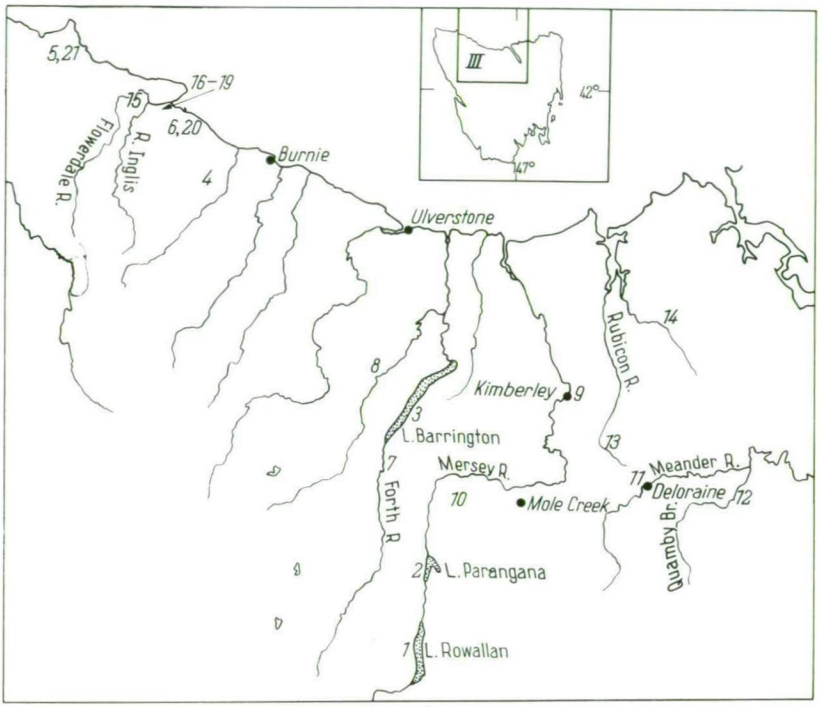

Fig. 6. The location of sample sites in Province III—the North-West of Tasmania.

The Ben Lomond massif is a special case within this Province. It is a high-elevation granite block capped with dolerite. Its waters (Table 4) (Samples 11–19,21) have seawater-type dominance orders typical of inert rocks, though there is some enrichment by calcium and bicarbonate. Not surprisingly, they resemble the waters of the western Central Plateau.

e) Province V — The Bass Strait Islands

The waters of the Bass Strait Islands (Fig. 8) present a range of types (Table 5) from dilute, acid, humic waters (Samples 1, 7, 8) with seawater dominance, through types with apparent geochemical influences, to the high salinity lagoons (Samples 6,13). The former are similar to the waters of the South-West and the Queensland coastal lagoons (BAYLY, 1964) while the colourless, high-salinity lagoons are like the saline lagoons of the Midlands. They are, however, dominated by bicarbonate, not chloride. Chain of Lagoons (Sample 2) appears to be sulphate dominated, the only such water in this survey. Although rare, sulphate dominance has been reported elsewhere (RODHE, 1949, TALLING and TALLING, 1965).

5. Discussion

In a recent paper GIBBS (1970) concluded that three major mechanisms control the chemistry of surface waters throughout the world — atmospheric precipitation, geochemical processes and evaporation-crystallisation. Each process leads to a well-defined type of water with a continuum of variation between the extremes.

Table 2. Chemical characteristics of surface waters of the Central Plateau of Tasmania. The sample numbers refer to the locations indicated in Figure 4. + indicates a trace, — indicates undetectable

Location	No.	TDS ppm	TFS ppm	K_{18} $\mu S \cdot cm^{-1}$	pH	Colour Pt units	NA^+	K^+	Ca^{++}	Mg^{++}	Cl^-	HCO_3^-	SO_4^{--}	SiO_2 ppm	Fe ppm
							←			μeq/l			→		
Lake Dove	1	17.0	7.9	12.4	7.0	20	48	10	40	25	97	15	45	1.2	—
Lake Ayr	2	28.6	17.8	31.3	7.1	< 5	83	10	135	75	75	156	26	3.4	—
Lagoon on Mt. Pillinger	3	21.4	12.4	21.9	7.3	< 5	78	8	75	50	83	91	24	2.3	—
Tarn on Paddy's Nut	4	20.6	4.4	12.6	6.8	20	44	10	65	25	103	23	18	0.7	—
Labyrinth No. 1	5	16.8	9.0	16.1	6.5	< 5	57	15	30	42	152	21	8	1.2	—
Labyrinth No. 2	6	18.4	11.2	13.3	6.6	< 5	52	18	25	25	83	20	7	0.3	—
Labyrinth No. 3	7	8.8	4.8	19.0	6.3	< 5	57	26	25	33	105	18	9	0.8	—
Labyrinth No. 3A	8	21.0	12.8	19.0	5.9	< 5	70	28	35	50	128	35	8	0.7	—
Labyrinth No. 4	9	20.2	11.4	13.9	6.1	< 5	48	18	35	33	64	30	12	1.4	—
Labyrinth No. 5	10	9.8	4.6	11.8	5.8	< 5	61	19	45	33	111	22	8	0.4	—
Lake Helios	11	11.4	7.0	16.8	7.4	< 5	44	5	40	67	109	17	16	1.3	—
Lake St. Clair	12	20.8	11.0	21.6	6.2	< 5	78	5	50	42	113	64	13	2.9	0.09
Lake Thor	13	13.0	9.2	15.5	6.9	< 5	48	20	50	25	60	60	19	1.2	—
Lake Salome	14	20.0	11.6	15.7	6.9	10	48	10	60	42	13	88	22	2.7	—
Lake Ball	15	16.0	8.8	17.8	7.6	5	48	12	45	33	54	79	19	1.1	—
Pool of Bethesda	16	20.0	15.2	23.2	6.8	< 5	52	13	90	66	49	143	45	4.0	—
"Lake Allison"	17	18.4	10.8	17.8	7.2	10	65	12	65	42	77	51	23	1.0	—
Lake Mackenzie	18	15.4	11.0	12.8	6.8	< 5	61	6	50	50	74	97	7	0.1	—
New Year Lake	19	21.8	12.2	21.5	6.9	< 5	96	5	90	67	92	135	7	0.5	—
"Lake Ivo"	20	17.0	8.4	19.3	6.9	< 5	65	5	70	58	81	80	7	0.1	—
Talinah Lagoon	21	17.8	14.0	20.0	6.7	< 5	52	8	95	67	70	120	38	0.5	—
Lake Ada	22	18.0	9.6	17.7	7.1	< 5	48	3	75	50	38	104	6	0.1	—
Carter's Lagoon	23	19.6	7.5	22.5	6.9	< 5	52	64	55	42	160	89	10	1.8	—
Lake Augusta	24	17.6	6.5	23.4	6.5	< 5	52	26	85	32	98	73	28	2.3	—
Pine Lake	25	12.7	6.3	14.8	7.8	< 5	30	15	45	17	50	34	21	1.6	—
Great Lake	26	20.1	9.0	20.1	6.3	< 5	57	8	69	60	73	110	11	1.2	—
Shannon Lagoon	27	25.7	16.1	38.6	7.3	< 5	96	8	135	184	140	281	38	7.1	—
Arthurs Lake	28	27.9	15.7	26.6	6.5	< 5	78	17	131	80	177	68	10	2.6	—
Little Lake	29	17.0	10.2	18.9	7.3	< 5	52	8	60	42	91	70	9	1.7	—
Gunn's Lake	30	18.6	12.6	16.3	7.4	< 5	57	15	60	33	63	95	11	3.3	—
Lake Echo	31	21.6	13.4	28.6	7.2	< 5	78	14	90	83	92	125	48	3.9	—
Bronte Lagoon	32	27.8	16.0	31.0	7.1	< 5	74	13	290	75	181	209	74	5.1	—
Tungatinah Lagoon	33	24.8	14.4	35.1	7.2	< 5	83	10	115	83	138	230	44	5.1	—
Lagoon of Islands	34	155.7	98.4	204.4	7.7	10	457	38	919	584	726	1422*	27	10.6	—
Woods Lake	35	58.7	41.6	57.3	7.1	< 5	148	16	162	110	242	368			0.14
Lake Sorell	36	57.8	41.8	51.2	7.0	< 5	187	18	189	138	200	300	90	12.9	1.56

Lake Crescent	37	61.2	42.9	86.0	7.0	< 5	278	20	211	203	469	300	40	—	0.08
Brownwater Lagoon	38	66.2	25.1	42.8	5.9	80	109	38	149	128	205	200	95	0.9	0.10
Iris River	39	28.4	18.4	27.7	7.2	< 5	87	5	70	75	171	115	8	5.1	—
Weaning Paddock Ck.	40	42.2	31.2	42.7	7.2	< 5	113	5	130	188	168	435*	6	10.4	—
Tarraleah Canal	41	24.8	8.5	27.4	5.5	15	96	17	32	23	230	104*	18	2.9	0.15
Ripples Ck.	42	35.4	24.2	35.3	7.4	< 5	96	14	131	70	48	456*	11	9.6	+
Lake River	43	75.4	44.6	111.5	7.9	< 5	174	18	650	320	129	1010	23	13.5	—
"Woods Ck."	45	65.0	37.6	68.7	7.4	15	165	19	242	185		960			0.22

* Bicarbonate reduced for further calculations.

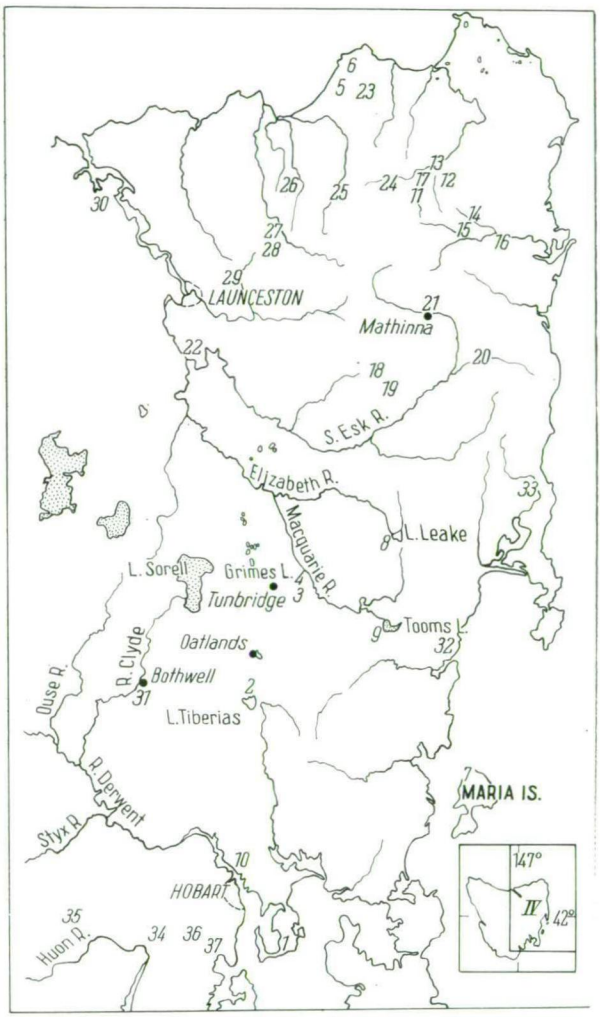

Fig. 7. The location of sample sites in Province IV—the Midlands, East and North-East of Tasmania

The small Australian state of Tasmania has sufficient climatic and ecological diversity to encompass these extremes and a wide range of intermediates. Our data supports in a general way GIBBS' notion of controlling mechanisms, and 2 Provinces are dominated by waters which are terminal types of the GIBBS distribution.

Over most of the South-West and West, waters have seawater ionic proportions, a characteristic of many waters draining peat bogs and heaths (GORHAM, 1955, 1958, 1961; TOLPA and GORHAM, 1961) and of waters receiving direct sea spray (BAYLY, 1964; TYLER, 1972). The predominance of this type of water in the South-West is determined by (a) high rainfall from prevailing south-westerly winds, (b) the predominance of highly stable quartz-alumina minerals in extensively metamorphosed rocks (SOLOMON, 1962), (c) resistance to

Table 3. Chemical characteristics of surface waters of the North-West of Tasmania. The sample numbers refer to the locations indicated in Fig. 6. + indicates a trace, – indicates undetectable.

Location	No.	TDS ppm	TFS ppm	K_{18} $\mu S \cdot cm^{-1}$	pH	Colour Pt units	Na^+	K^+	Ca^{++}	Mg^{++}	Cl^-	HCO_3^-	SO_4^{--}	SiO_2 ppm	Fe ppm
							←			μeq/l			→		
Lake Rowallan	1	26.5	15.6	25.2	6.2	< 5	61	9	115	63	90	163	11	4.8	0.05
Lake Parangana	2	22.1	12.8	20.7	6.2	< 5	52	6	140	58	120	131	26	4.4	–
Lake Barrington	3	32.6	21.0	32.2	6.3	< 5	96	18	110	100	117	180	39	4.1	–
Dam, Elliot Res. Farm	4	70.2	49.6	70.5	7.0	< 5	298	62	153	253	382	3860*	46		0.18
Dam, Detention	5	164.4	88.2	167.2	4.8	280	566	105	283	400	842	0	320	0.7	0.26
P. R. Bauld's Dam	6	58.2	35.4	76.1	7.0	5	231	68	131	198	415	1144*	18	9.8	–
Creek on Round Mt.	7	45.0	35.4	42.7	7.5	< 5	130	11	133	192	156	349	9	10.2	–
Castra Rvt.	8	32.8	23.0	40.6	7.5	20	118	18	110	133	186	201	21	4.1	–
Mersey River	9	108.8	71.8	173.6	7.8	5	139	23	750	283	179	1763*	36	5.8	–
Maracoopa Creek	10	78.6	53.8	113.6	7.7	< 5	104	13	1060	125	132	1151	25		–
Meander River	11	66.2	55.6	95.1	6.8	< 5	122	23	330	267	128	879*	29	6.1	–
Quamby Brook	12	162.2	72.4	142.5	7.0	15	295	31	280	616	469	1084*	36	10.0	–
Rubicon River	13	156.4	118.8	187.4	7.5	10	395	46	425	1125	581	1960*	43	20.0	–
Saxon's Creek	14	84.4	60.4	111.9	6.0	50	409	46	160	248	677	231*	71		–
Flowerdale River	15	74.6	43.4	84.5	5.8	70	283	58	140	225	480	940*	37		0.18
Big Creek	16	64.8	43.4	83.0	6.6	10	287	47	145	228	445	1223*	32		0.14
Inglis River	17	72.4	45.8	87.0	7.0	80	296	24	148	238	468	1021*	47	19.6	0.20
Blackfish Creek	18	81.0	56.6	110.2	6.6	< 5	387	65	158	253	644	1860*	32		+
Wilson's Creek	19	135.8	69.8	132.0	5.3	240	522	105	142	188	819	420*	81	2.0	0.58
Bauld's Creek	20	103.2	92.2	167.2	6.9	< 5	610	55	225	327	1019	2041*	73	8.8	–
Heath Drainage, Detention	21	193.4	92.6	182.3	4.8	560	610	105	55	277	1430	0	115	1.4	0.52

* Bicarbonate reduced for further calculation

Table 4. Chemical characteristics of surface waters of the Midlands, East and North-East Tasmania. Sample numbers refer to the locations indicated in Fig. 7. + indicates a trace, – indicates undetectable

Location	No.	TDS ppm	TFS ppm	K_{18} $\mu S \cdot cm^{-1}$	pH	Colour Pt units	Na^+	K^+	Ca^{++}	Mg^{++}	Cl^-	HCO_3^-	SO_4^{--}	SiO_2 ppm	Fe ppm
							←			$\mu eq/l$			→		
Calverts Lagoon	1						69510	2281	4400	20000					.15
Lake Tiberias	2	463.6	319.8		7.6	140	4350	1024	130	2166	7360	2160		–	–
Tunbridge No. 1	3	25092		59500	8.5	50	640000	2560	25000	142000	487000	9990	589	.6	.29
Tunbridge No. 4	4	86384		174500	8.3	20	810000	20500	350000	1600000	1587000	236	83900	.5	.95
Blackmans Lagoon	5	2381.0			8.2	70	11310	5	4050	6917	34400	5809	496		.30
Little L. Waterhouse	6	1253.2			7.9	60	9562	385	4450	4583	17320	3990*	940		–
Benachi's Creek Dam	7	238.4	191.6	363.2	8.3	5	930	48	1900	317	1425	237	70	18.0	–
Lake Leake	8	42.2	27.0	44.0	6.6	< 5	139	23	165	100	255	640*	13	7.6	–
Lake Tooms	9	32.1	22.1	24.6	6.8	< 5	161	38	108	113	261	156*	31	6.3	–
Risdon Brook Dam	10	90.8	68.5	132.2	7.1	< 5	278	31	465	776	460	150	600	4.5	–
Briseis Dam	11	34.6	21.4			20	165	15	50	58	269	34	40		.20
Frome Dam	12	43.4	31.2	52.1	7.3	40	244	18	55	100	443	45	28		.15
Cascade R.	13	39.2	29.8	56.4	7.3	< 5	213	21	70	108	355	144*	32		–
Groom R.	14	50.6	38.4	52.4	6.9	20	256	23	55	83	440	80	34		.10
N. George R.	15	41.2	33.6			< 5	218	15	95	125	343	200*	43		.10
George R.	16	44.4	34.4	59.0	7.9	< 5	244	28	85	142	342	312*	36		.10
Weld River (N. E.)	17	42.8	28.8	71.2	7.1	< 5	244	15	80	142	305	180	25	–	–
Story's Creek	18	18.8		21.4	6.7	5	50	17	105	63	56	139	45		–
Aberfoyle Creek	19	33.8		41.5	7.1	5	83	8	210	138	84	308	38		–
Break O'Day River	20	126.2		203.9	7.4	5	562	24	820	509	471	1070	95		.16
South Esk R., Mathinna	21	32.4		37.0	6.9	5	159	11	80	108	169	140	38		.20
South Esk R., Perth	22	80.0	51.6	91.0	5.7	20	250	40	229	250	440	1243*	49	10.9	–
Sheepwash Creek	23	244.4	173.4		7.1	120	1617	108	115	667	2874	121	110		.20
Ringarooma R.	24	58.4	47.2	66.6	6.8	< 5	261	33	100	117	407	104	16	9.2	–
Forester R.	25	42.0	32.0	46.3	6.8	< 5	183	33	70	92	274	187*	28	8.0	–
Brid. R.	26	56.4	40.4	57.8	7.0	< 5	218	31	105	108	340	200*	37	13	–
Crk. on Sideling	27	33.6	24.8	37.1	7.3	< 5	148	26	49	75	255	50	15	2.3	–
St. Patricks R.	28	38.0	26.4	39.4	6.9	< 5	144	15	90	83	180	152	23	10.1	–
Distillery Ck.	29	41.0	29.6	44.0	6.9	< 5	148	20	95	100	205	203	8	6.5	–
Blue Tier Ck.	30	177.0	132.0	245.0	6.9	60	935	82	750	605	1632	869*	70		–
Clyde River	31	128.4	91.4	181.0	7.5	20	530	45	750	467	1045	1550*	17	9.6	.16
Lisdillon River	32	174.4	152.5	252.3	7.0	40	1042	51	750	816	1294	1261	204	8.8	–
Apsley River	33	68.8	48.6	89.5	7.4	< 5	292	15	200	243	555	3860*	22		–
Mountain River	34	76.8	52.0	107.5	7.6	< 5	292	42	290	257	466	981*	42	11.7	.10
Russell River	35	51.4	33.2	61.7	7.6	5	183	16	189	195	310	710*	20		+
Sandfly Rvt.	36	86.8	62.2	111.6	7.5	30	379	38	245	258	605	352	64		–
N. W. Bay River	37	95.0	60.4	111.6	6.9	30	330	46	390	284	515	456	68		.05

* Bicarbonate reduced for further calculations

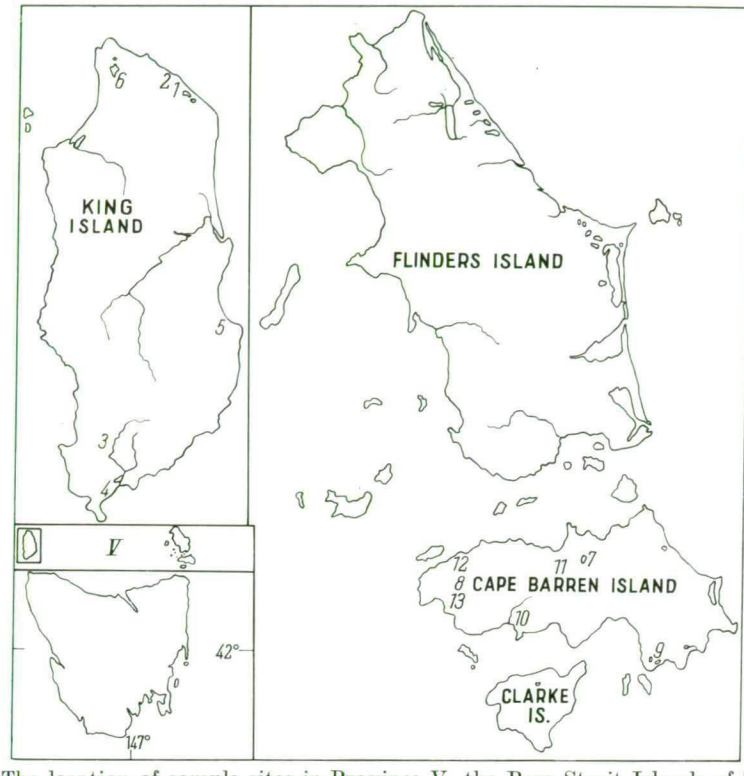

Fig. 8. The location of sample sites in Province V—the Bass Strait Islands of Tasmania

weathering of these rocks (HOLMES, 1965) and (d) the large areas of peat soil derived from *Gymnoschoenus sphaerocephalus* (Cyperaceae) which isolates the water from underlying rock. Supply of ions is mainly from airborne sea spray. The lack of significant geochemical influence can be gauged from the low silica concentrations.

Rock-dominance waters (the second terminal type of GIBBS) occur in all Provinces where easily-weathered rocks such as dolomite occur. Within the South-West, where seawater ionic proportions are usual, outcropping dolomite and serpentenite dramatically change the ionic composition as in the case of waters draining the northern slopes of Mt. Anne. The alkaline earth—bicarbonate dominance of such waters is usual wherever minerals are readily soluble in weakly acid rainfall (GORHAM, 1961 : HOLMES, 1965).

Most of Tasmania's dilute waters (< 800 ppm TDS) are intermediate between precipitation-dominant and rockdominant. The varying degrees of modification of seawater ionic proportions are shown by the ternary diagrams (Fig. 9). Waters on dolerite usually lie within the dotted line in the ternary diagrams (Fig. 9). Since dolerite is so abundant, most of Tasmania's lakes will be of this type.

Evaporation-crystallization processes lead to the third end type of the GIBBS scheme, where composition is determined by the ion source and by crystallization as concentration of saline waters proceeds. In Tasmania waters of this type are restricted to the Midlands and North-East in areas with high evaporation precipitation ratios so that closed lakes may occur (LANGBEIN, 1961). Even the magnesium chloride dominance of Tunbridge Lagoon No. 4 can be explained by this phenomenon.

Though the chemistry of Tasmanian waters is explicable in terms of the three processes outlined by GIBBS (1970) they do not fall entirely within the boomerang

Table 5. Chemical characteristics of surface waters of the Bass Strait Islands. The sample numbers refer to the locations indicated in Fig. 8. – indicates undetectable

Location	No.	TDS ppm	TFS ppm	K_{18} µS. cm^{-1}	pH	Colour Pt units	Na^+	K^+	Ca^{++}	Mg^{++}	Cl^-	HCO_3^-	SO_4^{--}	SiO_2 ppm	Fe ppm
							←			µeq/l			→		
King Island															
Lake Martha Lavinia	1	393.2	238.2	404.0	5.1	500	2175	100	245	866	3751	172	800	0.4	0.35
Chain of Lagoons	2	394.3	276.6	426.8	6.7	1000	2428	120	295	783	3920	468	4800	—	1.30
Pearshape Lagoon	3	279.9	210.4	367.7	7.0	250	1622	258	1690	700	3820	1055	704	—	—
Penny Lagoon	4	419.8	532.4		7.0	30	4173	269	365	1524	7755	525	3600	0.3	—
Naracoopa Rutile Dam	5	315.2	236.5	397.1	7.1	150	1588	95	340	759	3584	321	800	5.7	0.50
Lake Flanigan	6	1463.2	1249.3		8.8	40	8235	553	1900	4220	1884	3190	1035	0.1	0.15
Cape Barren Island															
Big Reedy Lagoon	7	538.4	—		5.3	600	4080	308	2200	1250	6610	0	509		0.50
Big Grassy Lagoon	8	214.2	128.4	234.0	5.7	400	1304	31	120	292	1763	71	140		0.80
Lagoon on Crows Pt.	9	834.6	—		7.0	30	8300	385	2250	200	12360	520	468		0.20
Creek at Half Moon Bay	10	243.6	183.4	306.0	7.0	200	2043	97	100	458	2747	167	115		0.30
Dover River	11	155.6	125.6	216.0	7.3	100	1645	62	85	350	1933	140	65		0.30
Home Hill Lagoon	12	563.8	460.2		7.3	350	5090	213	165	683	6070	753	381		0.50
Modder Lagoon	13	998.0	—		8.5	70	11420	385	4200	2167	7120	8782	511		—

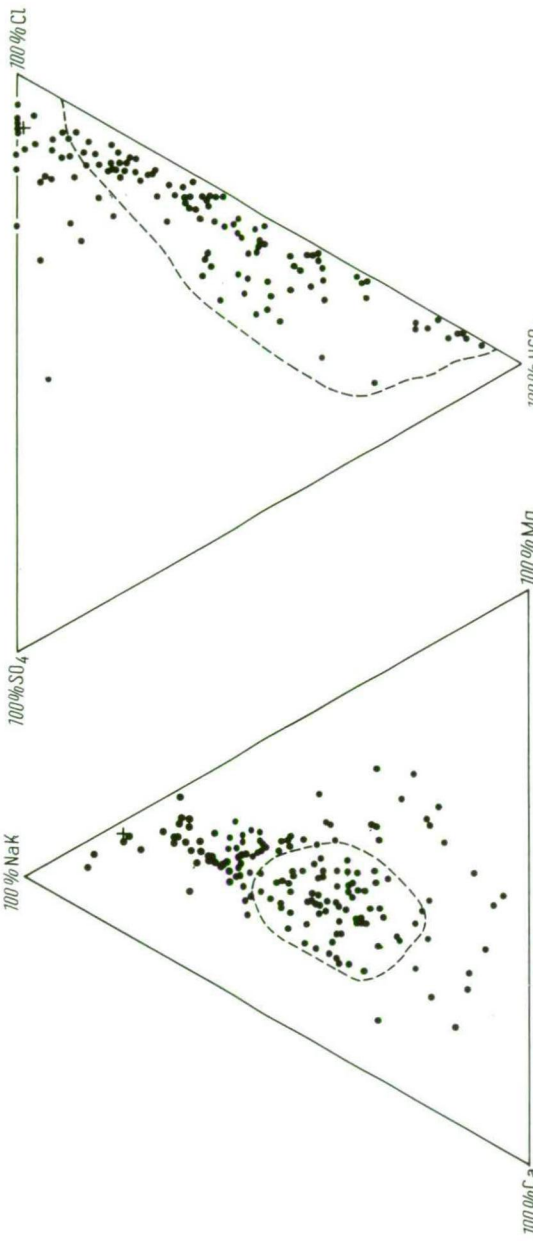

Fig. 9. Ternary diagrams showing ionic proportions of dilute (TDS < 800 ppm) Tasmanian waters sampled in this survey. Dilute dolerite waters lie within the dotted lines. + indicates seawater proportions.

distribution of his Fig. 1. Our data would fill in between the arms of the boomerang. A statement better describing the Tasmanian case is that when concentration increases beyond a certain value (c. 850 ppm TDS) the maximum attainable proportion of divalent ions decreases. At hypersaline concentrations, however, salting out of monovalent cations may lead to Mg or Ca dominance (e. g. Tunbridge No. 4).

The relationship between conductivity and total ionic concentration, TDS and TFS is approximately linear, the best correlation being between K_{18} and TFS where TFS = 0.5 K_{18}. Other relationships are TFS = 0.72 TDS and Σ^+ (μeq/l) = 8.8 K_{18}.

The relationships hold for waters with concentrations up to 300 mg/l. The only waters with greater concentrations are the saline lagoons and some Bass Strait Islands lagoons and for these the relationships have not been investigated. The contribution of organic matter to TDS values, and of the H^+ ion to conductivity, is significant in the case of dilute brown waters.

Silica concentrations in most lakes are low but in rivers they may be as high as 20 ppm. Rivers also tend to be more enriched in bicarbonate than do lakes and frequently display an anion excess. This may be caused by contribution of HCO_3^- in the solid phase (GOLTERMAN, 1969).

Tasmania is the richest state, limnologically, of the Commonwealth of Australia. It has most of the country's lakes and also a greater range of type than other states. It is the only state where glacial lakes are well developed. Whereas in most states saline or hypersaline waters predominate the vast majority of Tasmania's lakes are likely to contain less than 50 ppm TDS. It is a pure water state.

6. Acknowledgements

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Pollution of a Tasmanian River by Mine Effluents
I. Chemical Evidence

Abstract

Discharge of effluents from tin and wolfram mines has caused severe pollution of two creeks and lesser pollution of the South Esk River in North-East Tasmania. The principal pollutants are sulphuric acid, zinc, cadmium, copper, lead, iron and manganese in dissolved or particulate form or both. The creek waters are rendered unsuitable for domestic or agricultural use and all normal biota destroyed. In the South Esk River trout are absent from polluted reaches though abundant elsewhere. Flood-borne mine tailings, rich in particulate pollutants, have destroyed or degraded pastures along the South Esk River.

1. Introduction

In Tasmania, despite a short history of exploitation and a low human population density, some rivers are now polluted. This paper is concerned with the chemical evidence for river pollution (in the sense of COULSON and FORBES (KLEIN, 1962)) resulting from discharge of mine effluents in the north-east of the state, and its effect on trout populations. The following paper (THORP and LAKE, 1973) reports the changes brought about in other biotic communities. Similar documentation exists for many rivers in the world, but there is none for Tasmania, and only two for the Australian mainland (DOOLAN and SMYTHE, 1973; WEATHERLEY, BEEVERS and LAKE, 1967).

The localities investigated are Aberfoyle and Story Creeks and the South Esk River (Fig. 1). All lie in the Fingal Valley where tin and wolfram have been mined since the late nineteenth century (Figs. 2–3). Wolframite predominates at Storys Creek, tin at Aberfoyle. Concentrates are produced by physical and chemical treatment. Coarse tailings are dumped in heaps but finer slurry is piped to settle ponds, and supernatants are discharged into the creeks which eventually join the South Esk River. The effects of chief pollutants lead, zinc, copper, cadmium, manganese, iron and sulphuric acid extend far beyond the mine areas. Farmers bordering the creeks are unable to use the water, fish and other normal aquatic biota are absent from the creeks, and in polluted reaches of the South Esk River the biotic communities are changed (THORP and LAKE, 1973) and trout are no longer found. During floods mineral rich silts are deposited on the land with subsequent loss or degradation of pastures.

2. Materials and Methods

Samples were collected from the localities indicated in Figure 1. Water samples were collected in polyethylene bottles on one or more of the following dates: 14, 21, 22. V. 1970; 22, 23. X. 1970; 13. I. 1971. In addition, to indicate the nature of day-to-day variation in chemical composition,

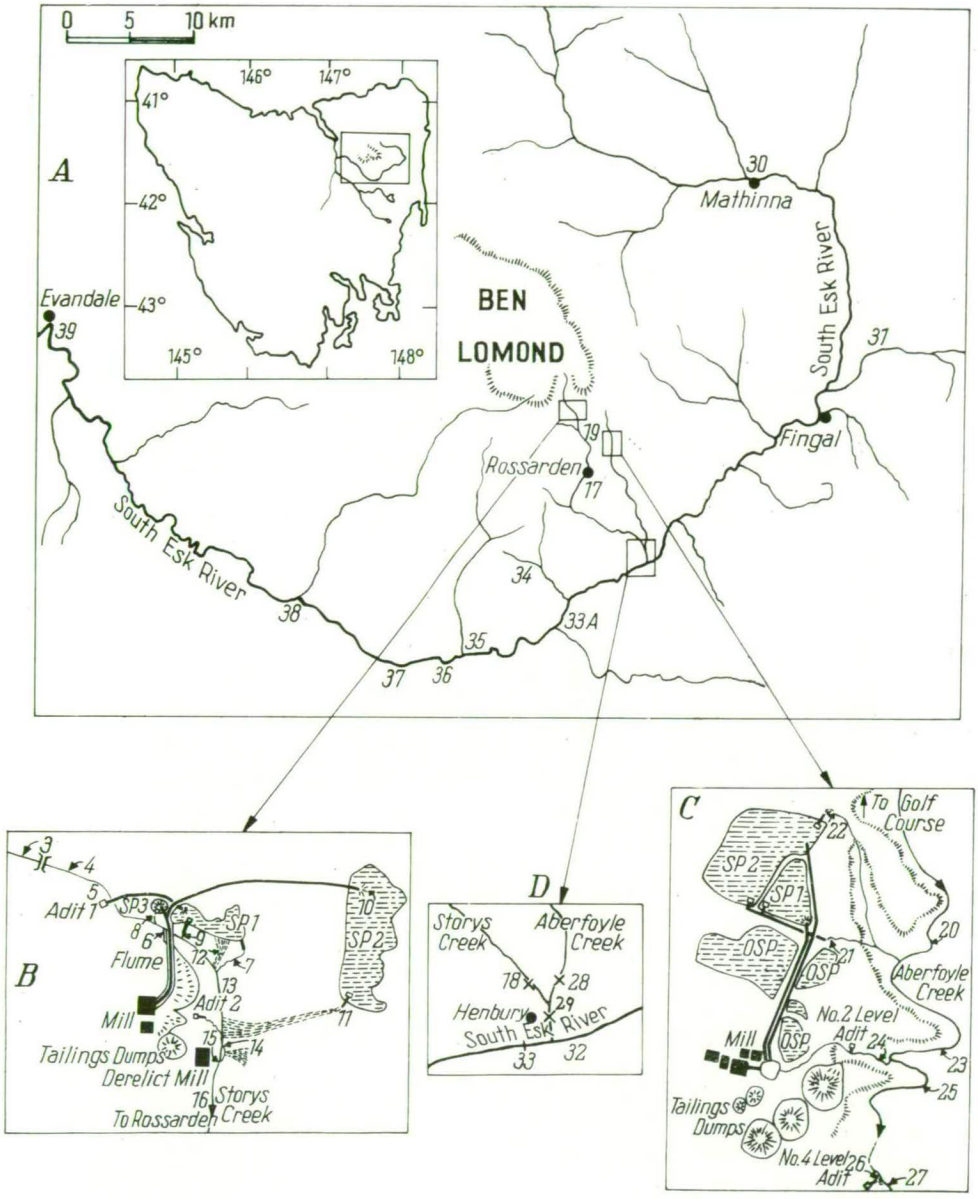

Figure 1. Map of the South Esk catchment (*A*), diagrams of Storys Creek (*B*) and Aberfoyle (*C*) mine areas, and detail of the entry of the creeks into the South Esk (*D*), showing sample sites. *SP* = settle pond. *OSP* = disused settle pond.

samples were collected from three localities (sample points 18, 28 and 29) over a 22-day period (28. V. 1970–17. VI. 1970). Silt samples were collected from Henbury in 1970 and Bonney Plains in 1969.

Turbidity was measured nephelometrically, pH electrometrically, colour with a Lovibond Nessleriser, and conductivity with a portable meter. Water samples were filtered through 0.5 μm membranes. Total suspended solids (TSS) were determined by weighing the dried residue. Analyses

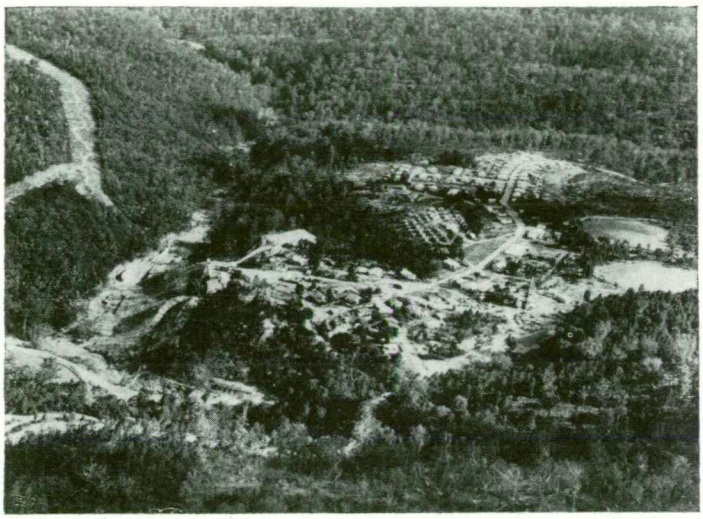

Figure 2. Aerial photograph of Storys Creek mine, from the north. Settle pond No. 1 is at the extreme left. The mill is left centre and the flume from the mill slants across the dumps and crosses the creek at the eastern end of the settle pond.

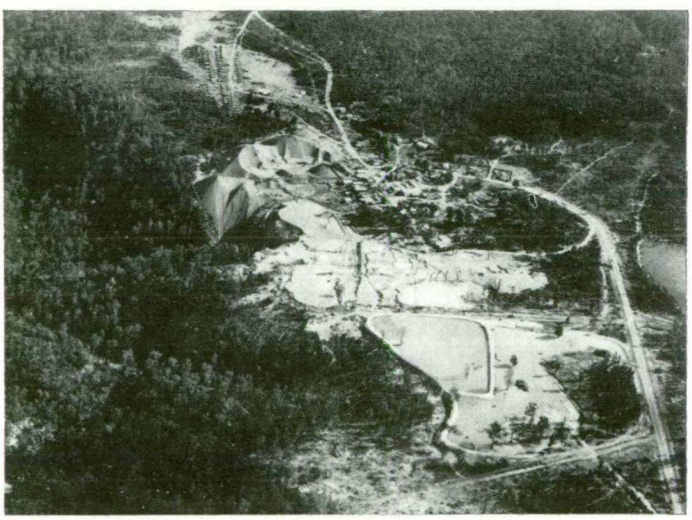

Figure 3. Aerial photograph of Aberfoyle mine, from the north.

were of filtered water and acid or alkaline digests of solids. Total dissolved solids (TDS) were determined by evaporation and sulphate by ion exchange procedures (MACKERETH, 1955). All cations were determined by atomic absorption spectroscopy using a Techtron AA 5 instrument. Releasing agents and ionization buffers were added when necessary. Alkalinity (HCO_3^-) was determined by titration.

The presence or absence of brown trout (*Salmo trutta* L.) and eels (*Anguilla australis occidentalis* SCHMIDT) was investigated by electro-fishing, and the toxicity of Storys and Aberfoyle Creeks to fish by confining small brown trout in these waters for various periods of time in April 1970. These investigations were made by the Inland Fisheries Commission of Tasmania.

3. Results

Analyses of effluents and water samples are shown in Tables 1–3 and Figure 4. Fuller analyses of unpolluted river and creek waters in the area are given by BUCKNEY and TYLER (1973). Analyses of suspended solids and silt samples are given in Tables 4 and 5 respectively. Table 6 gives the results of *in situ* tests of toxicity to fish of Aberfoyle and Storys Creeks.

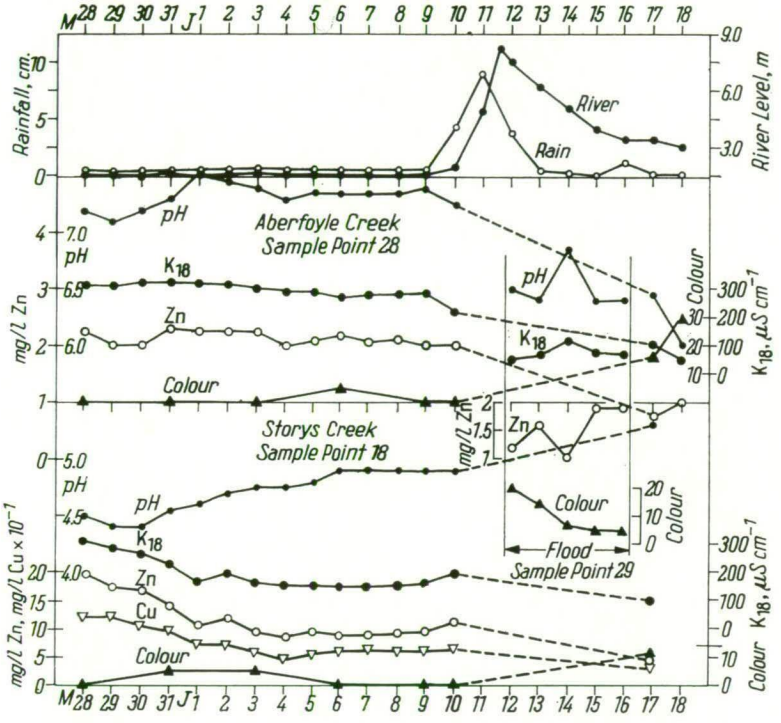

Figure 4. Concentrations of zinc, copper and other chemical parameters in Storys Creek and Aberfoyle Creek at Henbury, 28. V. 70–18. VI. 70.

4. Discussion

The survey clearly showed the abrupt changes in water quality brought about by mine water, settle pond effluents and unsettled slurry from crushing mills in the area investigated. At Storys Creek the native water (sample point 3, Table 1) was clear with the low TDS, conductivity values and ionic concentrations typical of unpolluted mountain creeks on dolerite (BUCKNEY & TYLER, 1973). Traces of native copper, zinc and manganese below measurable quantities were also detected. Downstream, some increase in sulphate, zinc, cadmium and copper concentrations began at sample point 4 (probably from seepage), but marked increases of these ions, and of manganese and iron, occurred further downstream after entry of effluents rich in pollutants from settle ponds, adits and a flume (Fig. 1 and Table 1). The effect of sulphuric acid could be seen in lowered pH, increased sulphate concentration and

Table 1. Chemical composition of mine effluents and of water samples from Storys Creek. An asterisk indicates a trace beyond measurement was detected

Sample Point[1]	Date	Turb. (J. T. U.)	TSS (mg/l)	TDS (mg/l)	K_{18} ($\mu S \cdot cm^{-1}$)	pH	HCO^{3-}	SO_4^{2-}	Zn^{2+}	Cd^{2+}	Cu^{2+}	Fe^{2+}	Mn^{2+}
									(mg/l)				
3	14/5/70			19.0	23.2							0	
3	21/5/70		0	18.8	21.4	6.7	8.5	2.2	*		*	0	*
4	22/5/70	1.2			23.5	7.1	11.3	7.1	0.10	0.03	0.02	*	*
5	22/5/70	195			1785	4.9	0	528	105	6.10	1.35	20.50	22.50
6	22/5/70	57			1418	4.8	0	362	77.0	4.20	0.85	15.75	15.80
7	21/5/70		8.6	586	905	4.5	0	156	46.50		0.60	9.00	9.00
7	22/5/70	41			960	5.1	0	253	50.0	2.60	0.45	7.20	10.30
8	22/5/70	210			63.70	6.8	8.8	77.8	0.72	0.06	*	0	0.50
9	22/5/70	410			81.1	7.0	15.6	96.5	0.65	0.05	0.07	0.20	0.60
10	13/1/71	210			86.2	6.9	12.1	76.8	0.38	0.03	*	0	0.60
11	13/1/71	17			114	5.8	0	71.0	1.39	0.06	0.05	5.40	0.80
12	21/5/70			806	1780	3.1	0	216	35.70		2.20	15.70	10.50
13	14/5/70			641	1036			161	43.00		0.60	0.50	
14	21/5/70			66.6	85.9	5.3	1.2	13.4	4.00		0.20	*	0.35
15	21/5/70		632	361	620	3.7	0	40.2	28.00		2.40	0.90	4.70
16	22/5/70	199			399	4.8	0	147	25.00	1.30	1.35	4.65	5.10
17	21/5/70		2.6	156	206	4.7	0	35.5	12.00		1.00	0.10	1.65
17	22/5/70	17			89.1	6.1	2.4	116	3.70	0.16	0.25	0.25	0.50
18	14/5/70			154	194			30.7	12.20		0.75	0.20	1.65
18	21/5/70		0.05	152	196	4.6	0	34.8	11.70		0.85	0.27	1.60
18	23/10/70	14			104	6.1	3.1	156	5.84	0.25	0.25	0.20	0.75
18	13/1/71	3				5.4	0.9		7.3	0.21	0.38		

[1] Location of sample points indicated in Fig. 1.

Table 2. Chemical composition of mine effluents and of water samples from Aberfoyle Creek. An asterisk indicates a trace beyond measurement was detected

Sample Point[1]	Date	Turb. (J. T. U.)	TSS (mg/l)	TDS (mg/l)	K_{18} ($\mu S \cdot cm^{-1}$)	pH	HCO^{3-}	SO_4^{-2}	Zn^{2+}	Cd^{2+}	Cu^{2+}	Fe^{2+}	Mn^{2+}
										(mg/l)			
19	21/ 5/70		2.2	33.8	41.5	7.1	18.8	1.8	*		*	*	0.12
20	21/ 5/70		4.7	34.4	49.7	7.1	19.5	2.2	*		*	0.20	*
21	14/ 5/70			82.4	126			17.8	0.50			0.10	1.70
21	21/ 5/70		127	82.2	145	6.8	12.8	16.3	0.25		*	0.10	1.15
21	23/10/70	27			221	7.6	24.5	96.0	0.12	0.03	0.07	*	0.60
22	23/10/70	30			232	9.0	26.7	97.0	0.11	0.03	0.10	0	0.40
23	23/10/70	5			77.3	7.6	22.6	71.5	0.30	0.03	0.07	*	0.07
24	21/ 5/70		60	920	1297	6.2	7.3	254	11.25		1.00	*	3.80
24	23/10/70	5			1649	6.2	4.1	537	17.00	0.70	2.35	0.10	4.25
25	23/10/70	6			113	7.5	23.2	72.0	0.65	0.04	*	*	0.20
26	23/10/70	55			1182	8.1	223	230	4.81	0.21	0.07	*	2.25
26	13/ 1/71						202		4.30	0.25	0		
27	23/10/70	11			269	7.8	49.3	113	1.7	0.08	0.05	*	0.50
28	14/ 5/70			207	296			52.8	2.4		*	*	0.10
28	21/ 5/70		2.7	228	302	7.1	36.0	49.0	2.4		*	0.05	0.06
28	23/10/70	5.4			231	7.5	32.5	166	1.69	0.10	0.18	*	0.15
28	13/ 1/71						34.6		1.29	0.03	*		

[1] Location of sample points is indicated in Fig. 1.

Table 3. Chemical composition of water from combined Storys and Aberfoyle Creeks and from the South Esk River and its tributaries. An asterisk indicates a trace beyond measurement was detected

Sample Point [1]	Date	Turb. (J. T. U.)	TSS (mg/l)	TDS (mg/l)	K_{18} ($\mu S \cdot cm^{-1}$)	pH	HCO^{3-}	SO_4^{2-}	Zn^{2+}	Cd^{2+}	Cu^{2+}	Fe^{2+}	Mn^{2+}
										(mg/l)			
30	21/ 5/70		0	32.4	37.0	6.9	8.6	1.8	*		*	0.20	0.01
31	21/ 5/70		0.9	126	204	7.4	65.3	4.6	*		*	0.16	0.02
32	23/10/70	3.7			66.4	7.4	17.2	2.9	*	*	*	0.10	*
32	13/ 1/71						21.7		*	*	*		
29	23/10/70	13			136	6.7	7.3	126	4.09	0.21	0.25	*	0.60
29	13/ 1/71						9.2		4.34	0.13	0.15		
33	14/ 5/70			52.8	72.7			2.8	0.50			0	0.01
33	21/ 5/70		5.4	52.0	66.5	7.0	14.0	2.2	0.30			0.16	0.03
33	21/ 5/70		5.3	52.2	65.2	7.0	12.8	3.1	0.30		*	0	0.01
33	23/10/70	5			76.0	7.5	17.0	6.1	0.38	0.04	0.10	0.10	0.07
33	13/ 1/71						21.7		0.15	*	0.10		
33A	13/ 1/71					7.5	21.7		0.15	*	0.10		
34	21/ 5/70		1.0	39.6	42.7	6.3	1.2	2.1	*		*	0	0
35	22/10/70	23			287	7.8	90.0	116	0.12	0.04	0.20	*	*
36	23/10/70	4.7			105	7.5	24.7	6.2	0.26	0.04	0.15	0.10	0.07
37	21/ 5/70		4.5	58.6	81.5	6.9	20.1	2.7	0.25		*	*	0.01
38	23/10/70	3.4			102	7.5	26.5	6.7	0.24	0.04	0.10	*	0.05
38	13/ 1/71						25.0		0.09	*	0.10		
39	23/10/70	6.9			108	7.5	29.1	4.8	0.14	0.03	0.05	0.20	*
39	13/ 1/71						27.5		0.05	*	0.10		

[1] Location of sample points is indicated in Fig. 1.

Table 4. Chemical composition of suspended solids in effluents, Storys and Aberfoyle Creeks, and the South Esk River. Data expressed as mg/l of original sample water

Sample Point [1]	Date	Zn^{2+}	Cd^{2+}	Cu^{2+}	Pb^{2+}	Fe^{2+}	Mn^{2+}
7	21/5/70	0.14		0.08	0.30	5.60	0.04
8	13/1/71	56.20	2.60	8.40	11.20	750	9.80
9	13/1/71	77.80	3.60	12.30	19.00	750	28.50
15	21/5/70	2.80		1.64	0.50	55.80	1.56
17	21/5/70	0.04		0.08	0.40	1.26	0
18	21/5/70	0.02		0.06	0.20	0.40	0
21	21/5/70	0.66		0.26	0.36	9.40	0.56
24	21/5/70	0.64		2.08	0.60	5.80	0.28
28	21/5/70	0.04		0.04	0.30	0.24	0.02
33	21/5/70	0.12		0.04	0.28	1.12	0.06
33	21/5/70	0.10		0.06	0.18	0.98	0

[1] Location of sample points is indicated in Fig. 1.

Table 5. Some chemical constituents of South Esk flood plain silt, compared with normal soil. Data in ppm of soil sample

Sample point [1]	Zn^{2+}	Cd^{2+}	Cu^{2+}	Pb^{2+}
Henbury, nr. No. 29	1500		700	1500
Bonney Plains nr. No. 36	4060	153	1986	1444
Normal soil [2]	10—300	$\gtrsim 1$	2—100	2—200

[1] Location of sample points is indicated in Fig. 1.
[2] SWAINE, 1955.

Table 6. Mortality of small brown trout (*Salmo trutta* L.) confined in Storys and Aberfoyle Creeks, April 1970

Sample point [1]	Number of fish	Duration of confinement (hrs.)	Percent mortality
Storys Creek			
3	10	74	0
13	14	19	100
Aberfoyle Creek			
20	8	25	0
23	10	24	10
25	10	18	100
25	5	10	100

[1] Location of sample points is indicated in Fig. 1.

the zero alkalinity. Particulate material, as well as greatly increasing the turbidity, contained metallic pollutants (Table 4) which could later dissolve from the creek bed after settling.

A similar picture emerged at Aberfoyle Creek but with lesser severity apparently because addition of lime to settle ponds ameliorated the effects of sulphuric acid, and

reuse of settle pond effluents minimised effluent discharge. Above the entrance of water from mine sources (sample points 19 and 20, Table 2) the creek was clear with low TDS and conductivity values and low concentrations of ions, particularly zinc, copper, iron and manganese. After receiving effluents from the mine (sample point 21 et seq.) strong increases in turbidity, conductivity, TSS, TDS, sulphate, zinc, cadmium, copper, iron and manganese were evident.

In the South Esk River above the point of entry of water from Storys and Aberfoyle Creeks (sample points 30, 31, 32; Fig. 1 and Table 3), water quality was variable depending on location but in all cases zinc, cadmium and copper concentrations were extremely low. After receiving water contributed by the two creeks, the concentrations of these ions in the South Esk River rose considerably. The total pollutional load on the South Esk at this point is indicated by the analyses for sample point 29 (Table 3). Gipps Creek contributed small amounts of metal ions to the river (sample point 35, Table 3). Mining has been carried out at Gipps Creek for some time.

The amount and composition of effluent discharged depend on amounts of ore treated and on the particular process occurring at any given time, and the results in Table 1 show that considerable temporal variation occurred in the composition of effluents and polluted creek waters. Figure 4, however, shows that at Henbury there was little day-to-day variation during the period before the flood of 12–17 June. Presumably mixing and dilution effects in the several kilometres of creek smoothed out short term fluctuations. The significant fact is that zinc concentrations of 10–20 mg/l and copper concentrations of 0.5–1.0 mg/l were sustained in Storys Creek at Henbury over that period. These concentrations are of the same order as in other samples taken on widely separated dates (Table 1). Over the same period concentrations of zinc in Aberfoyle Creek at Henbury remained more or less constant at about 2 mg/l, a figure agreeing with analyses on other dates. Copper was present in low concentrations only. It is clear that pollution of Aberfoyle Creek was less severe than that of Storys Creek.

By all international standards, during the study period water from Storys Creek was unsuitable for domestic or agricultural use (Table 7); copper, cadmium and zinc concentrations were all undesirably high. In terms of zinc alone, the less polluted water of Aberfoyle Creek met international standards for most domestic and agricultural purposes, but cadmium and to some extent copper concentrations were excessive. The quality of water in both creeks was too poor for the survival of brown trout as shown by the results given in Table 6, and for the development of a typical benthic invertebrate fauna (Thorp & Lake, 1973). Benthic algae were uncommon in the creeks, except where diluted by unpolluted water as at sample point 14 where *Ulothrix* sp. grew healthily in a pool containing 4 mg/l Zn.

Considering the potability of water in the South Esk River, international standards for drinking water were met with the possible exception of cadmium concentrations (Tables 3 and 7). The analyses revealed cadmium concentrations on 23. X. 1970 higher than acceptable by world standards. While analysis by atomic absorption at such low levels was difficult, measurable quantities nonetheless entered the South Esk River from Storys and Aberfoyle Creeks. The results suggest the need for comprehensive examination of cadmium concentrations in the South Esk River using more sensitive analytical methods. Traces of metal pollutants were detected as far downstream as Evandale (Fig. 1). The data of Thorp & Lake (1973) also show that the effects of pollution extended this far. Electro-fishing showed that brown trout were absent from the South Esk from the point of entry of Storys and Aberfoyle Creeks to the vicinity of Evandale, though eels were present. Brown trout were common in the South Esk above and below the polluted reaches. The sensitivity of salmonid fish to metal toxins is well known. Though concentrations of zinc, copper

Table 7. Concentrations of some substances affecting water quality in Aberfoyle and Storys Creeks and in the South Esk River, compared with published standards. An asterisk indicates a trace below measurement

Water or Standard	TDS (mg/l)	pH	Zn^{2+} (mg/l)	Cd^{2+} (mg/l)	Cu^{2+} (mg/l)	Fe^{2+} (mg/l)	Mn^{2+} (mg/l)
Natural waters							
Storys Creek at Henbury	152—154	4.6—6.1	5.84—20.00	0.25	0.25—1.40	0.20—0.27	0.75—1.65
Aberfoyle Creek at Henbury	207—228	7.1—7.5	1.69— 2.40	0.10	*—0.18	*—0.31	0.06—0.15
South Esk River polluted reaches	52—59	6.9—7.5	0.14— 0.50	0—0.04	*—0.15	0—0.20	*—0.07
Standards							
FWPCA[1] (Public water supplies)	50—250	6.0—8.5	*— 5.0	0.01	*—1.0	*—0.30	*—0.05
WHO[2]	500—1500		5.0 —15.0	0.01	1.0 —1.5	0.30—1.00	0.10—0.50
USPHS[3]	500		5.0	0.01	0.05	0.30	0.05

[1] Federal Water Pollution Control Administration (1968).
[2] World Health Organization (1963).
[3] U. S. Public Health Service (1962).

and cadmium in the South Esk were low and perhaps below the incipient lethal level for brown trout, they greatly exceeded concentrations known to deter salmonids (SPRAGUE, ELSON & SAUNDERS, 1965).

With regard to the damage caused to pastures along the South Esk River by deposition of mineral-rich silt during floods, the concentration of metal pollutants in silt from riverside pastures along the South Esk was compared with the range of concentration of these elements in normal soil (Table 5). The much higher values in the silt samples were obvious and clearly implicated the silt as the cause of the damage to pastures. There were also generally high concentrations of these elements in suspended solids in mine effluents, Aberfoyle and Storys Creeks, and in the South Esk River (Table 4).

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Reconnaissance Limnology of Sub-Antarctic Islands II.* Additional Features of the Chemistry of Macquarie Island Lakes and Tarns

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Abstract

Further analyses of waters from lakes and tarns on Macquarie Island, including some not previously sampled, confirm conclusions of an earlier survey. Oceanic spray is a principal source of ions. Geochemical influence is minimal in most lakes, but Square Lake and Waterfall Lake contain considerably more calcium than others and the cationic dominance order is changed from that of seawater. Skua Lake is similarly affected though calcium concentrations are not so markedly increased. Magnesium enrichment does not occur.

Though calcium and bicarbonate accrue in approximately equivalent amounts, more lakes are deflected from seawater anionic dominance order than the three with changed cationic orders. Despite equivalent accession of calcium and bicarbonate, Square Lake and Waterfall Lake occupy anomalous positions on a plot of calcium proportions against Oceanic Origin Factor.

Seasonal variation in chemical composition is slight, but is greatest in Waterfall Lake and least in the shallow Square Lake where perhaps buffering by sediments is involved. Atmospheric supply of oceanic ions is commonplace on Sub-Antarctic islands.

Recent studies have shown that the water chemistry of lakes and tarns on Macquarie Island is controlled largely by the influx of oceanic spray, with geochemical weathering playing a minor role (Evans 1970; Tyler 1972). Some further analyses are now to hand which in part relate to lakes and tarns not previously sampled, and which also indicate some features of seasonal variation of water chemistry. These additional analyses form the basis of the present paper and supplement the data given by Tyler (1972).

Samples were collected in polyethylene bottles at various times of the year and stored on Macquarie Island until December 1971. They were then taken to Tasmania and stored at 4°C for 6–12 months before analysis by the methods described previously (Tyler 1972).

The locations of lakes sampled are shown in Fig. 1. Some lakes and tarns sampled for the first time are illustrated in Fig. 2. Chemical composition and derived properties of the waters are presented in Table 1.

Analyses of further samples of lake and tarn waters from Macquarie Island confirm earlier indications (Tyler 1972) that their chemical composition is that of air-borne sea spray minimally modified by geochemical weathering processes. Specific points of confirmation, and further conclusions from additional lakes sampled, are listed below.

(1) Comparison of analyses reveals only minor differences for lakes sampled in both investigations.

* Part I, *Int. Rev. ges. Hydrobiol.*, 1972, 57, 759–78.

(2) Square Lake and Waterfall Lake differ from most others in having considerably higher calcium concentrations, sufficient to change the cationic dominance order from that of seawater to Na > Ca > Mg > K. Skua Lake also has this dominance order though calcium does not greatly exceed magnesium in this case.

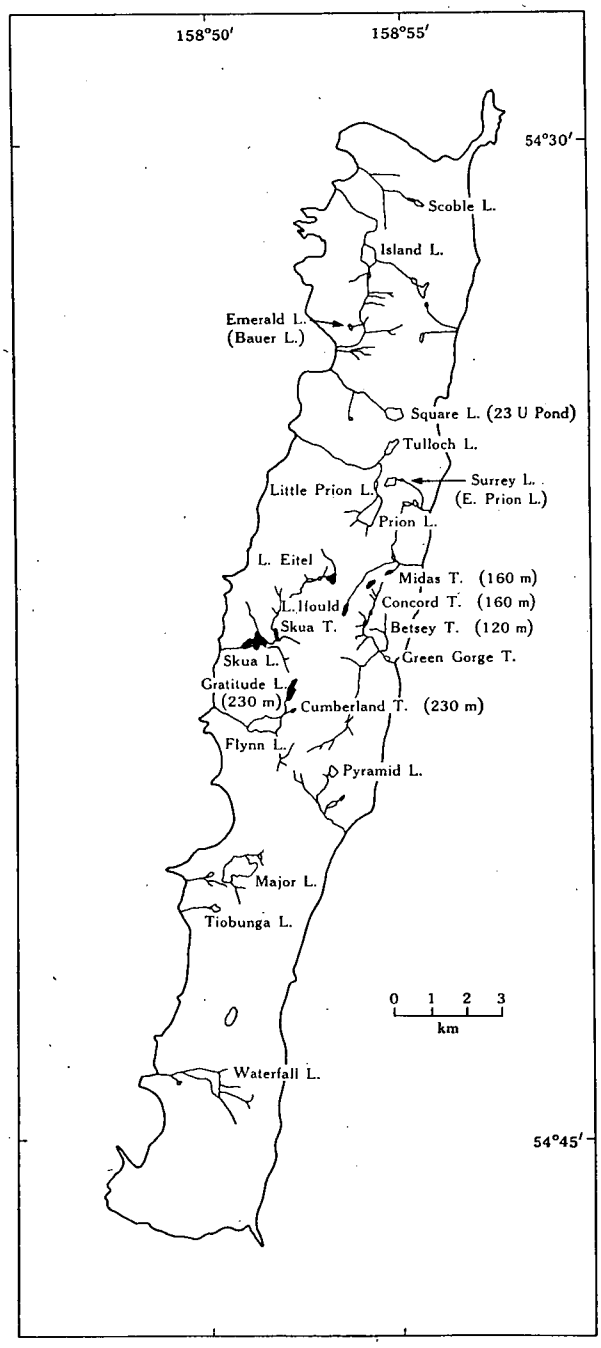

Fig. 1. Map of Macquarie Island showing sample sites. Lakes and tarns sampled for the first time are shown in black and their approximate altitude is shown. All names have Nomenclature Board of Tasmania approval. Rejected names, used previously, are shown in brackets.

(3) Square Lake, Waterfall Lake, Scoble Lake, Flynn Lake, Green Gorge Tarn and, additionally, Skua Tarn, Skua Lake, Gratitude Lake and Lake Ifould are deflected from seawater anion order by HCO_3^- becoming second dominant. From the previous analyses, Surry Lake (= Bauer Lake), Island Lake and Major Lake are also in this category.

(4) Points representing cationic or anionic proportions of lakes sampled in both series lie close together on ternary diagrams (Fig. 3), and Oceanic Origin Factors are similar though the values for the second series are a few per cent lower in most cases. This may result from the longer storage period before analysis of the second series of samples, allowing release of sulphate and or bicarbonate from particulate material.

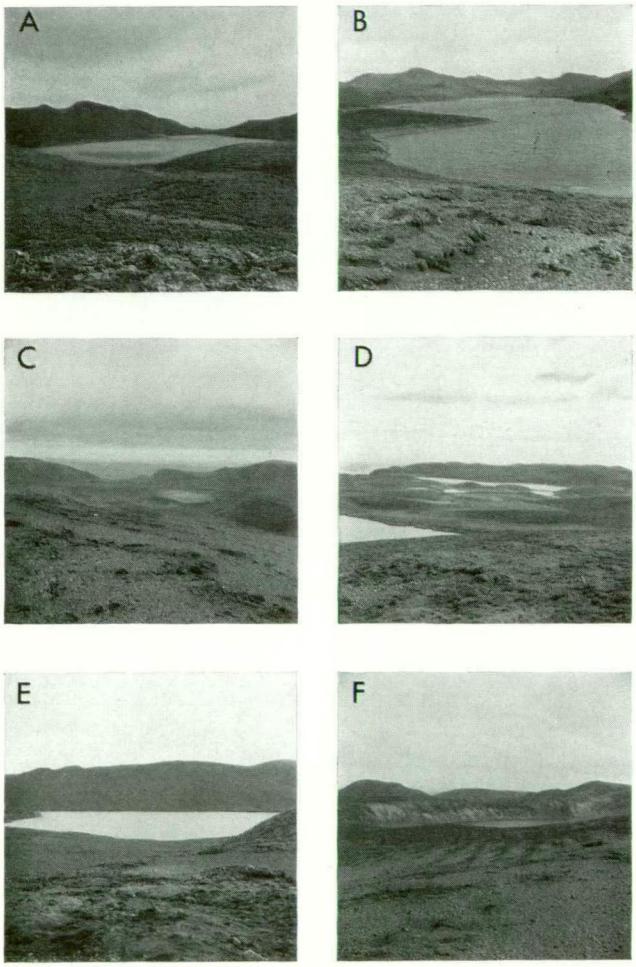

Fig. 2. Lakes and tarns of Macquarie Island.
A, Flynn Lake from Cumberland Tarn;
B, Gratitude Lake from the North;
C, Concord Tarn from Lake Eitel;
D, Skua Lake from Gratitude Lake;
E, Lake Eitel from the east;
F, Lake Ifould from the north.

(5) The ionic concentrations of Na^+ and Cl^- show strong positive correlation, the sodium : chloride ratios ranging from 0·68 to 1·31. This is a wider spread than the range 0·77–0·93 obtained by Tyler (1972), and the usual tendency for Na^+ to be in excess of that expected from the seawater ratio of 0·86 is more obvious.

(6) When the ionic proportion of Ca^{2+} is plotted against Oceanic Origin Factor (O.O.F.), most lakes occupy a position on the line fitted to Fig. 19 of Tyler (1972).

Table 1. Chemical characteristics of lake and tarn waters of Macquarie Island

Location	Date	K_{18} (μS/cm)	pH	Turbidity (J.T.U.)	Colour[a]	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	SiO_2 (mg/l)	$\Sigma^+ + \Sigma^-$ (m-equiv./l.)	O.O.F. (%)
						←			m-equiv./l.			→			
Scoble L.	27.xi.71	179	7·26	0·85	40	1·347	0·049	0·115	0·400	0·286	1·255	0·259		3·711	77·18
Square L.	2.vi.71	255	7·09	1·6	—	1·678	0·042	0·835	0·558	0·848	1·740	0·277	3·6	5·978	67·24
	9.vii.71	242	7·77	0·71	—	1·578	0·034	0·805	0·538	0·902	1·679	0·283	3·3	5·219	67·25
	26.xi.71	289	7·77	1·2	20	1·521	0·027	0·725	0·575	0·843	1·642	0·281		5·614	65·71
Tulloch L.	2.vi.71	158	6·61	0·38	—	1·248	0·033	0·102	0·299	0·081	1·310	0·260	1·1	3·333	87·84
	9.vii.71	152	6·41	0·96	—	1·257	0·033	0·100	0·290	0·075	1·234	0·251	0·8	3·240	87·56
	26.viii.71	147·8	6·66	0·90	—	1·174	0·036	0·097	0·283	0·102	1·189	0·259	1·6	3·140	84·92
	26.xi.71	140	6·41	0·70	5	1·218	0·030	0·093	0·258	0·073	1·081	0·248		3·001	85·35
Prion L.	2.vi.71	148·1	6·53	0·56	—	1·222	0·027	0·092	0·270	0·082	1·258	0·255	0·9	3·206	87·31
	9.vii.71	144	6·68	0·35	—	1·130	0·024	0·098	0·260	0·093	1·275	0·259	0·4	3·139	86·76
	26.viii.71	147·5	6·71	0·50	—	1·183	0·024	0·098	0·269	0·101	1·250	0·251	1·4	3·176	86·38
	26.xi.71	140	6·64	0·31	5	1·042	0·026	0·083	0·283	0·079	1·188	0·224		2·925	88·21
Midas T.[b]	26.xi.71	131	6·89	1·2	40	0·956	0·035	0·125	0·304	0·199	1·042	0·266		2·911	76·54
Concord L.[b]	26.xi.71	118	6·18	1·6	5	1·195	0·027	0·103	0·250	0·172	0·914	0·240		2·901	76·31
Betsey T.[b]	26.xi.71	116	6·67	0·65	5	0·870	0·029	0·095	0·232	0·126	1·014	0·240		2·606	81·34
L. Ifould[b]	26.xi.71	176	7·55	0·35	5	1·195	0·026	0·083	0·223	0·452	1·134	0·249		3·362	68·41
L. Eitel[b]	26.xi.71	161	7·16	1·6	5	0·869	0·027	0·115	0·321	0·221	0·994	0·241		2·788	75·57
Skua T.[b]	26.xi.71	205	7·34	4·2	5	1·219	0·031	0·295	0·350	0·389	1·451	0·270		4·005	76·13
Skua L.[b]	26.xi.71	224	7·75	0·87	5	1·240	0·022	0·377	0·320	0·575	1·348	0·259		4·138	68·32
Gratitude L.[b]	26.xi.71	165	7·26	0·4	5	1·021	0·023	0·185	0·308	0·250	1·189	0·249		3·225	77·98
Cumberland T.[b]	26.xi.71	128	6·06	2·6	5	0·761	0·021	0·058	0·208	0·048	1·122	0·245		2·463	87·77
Flynn L.	24.x.71	176	7·18	0·75	—	1·343	0·028	0·208	0·313	0·258	1·373	0·251	1·5	3·774	80·76
	26.xi.71	193	7·25	0·60	5	1·240	0·031	0·170	0·326	0·278	1·368	0·260		3·673	79·45
Green Gorge T.	26.xi.71	191	7·52	6·00	50	1·261	0·033	0·180	0·316	0·388	1·274	0·276		3·728	72·77
Pyramid L.	6.vii.71	123	6·19	2·8	—	0·996	0·022	0·092	0·230	0·057	1·072	0·249	2·0	2·718	86·11
	26.xi.71	127·5	6·26	1·8	5	1·064	0·024	0·064	0·234	0·058	1·025	0·250		2·719	85·12
Major L.	25.x.71	215	6·44	0·97	—	1·639	0·041	0·209	0·412	0·141	1·780	0·270	0·9	4·492	89·93
Tiobunga L.	25.x.71	184	6·25	1·1	—	1·435	0·036	0·105	0·323	0·051	1·554	0·272	0·6	3·776	91·65
Waterfall L.	6.vii.71	192	7·49	0·82	—	1·326	0·023	0·530	0·271	0·281	1·372	0·260	4·4	4·063	79·39
	29.x.71	198	6·85	0·9	—	1·426	0·023	0·645	0·285	0·399	1·450	0·272	7·8	4·500	75·67
Rain, isthmus	26–28.xi.71	62·0	6·87	—	—	0·344	0·013	0·041	0·083	0·075[c]	0·356	0·050		0·962	81·93

[a] Expressed as mg l^{-1} Pt. [b] Sampled for the first time. [c] By difference.

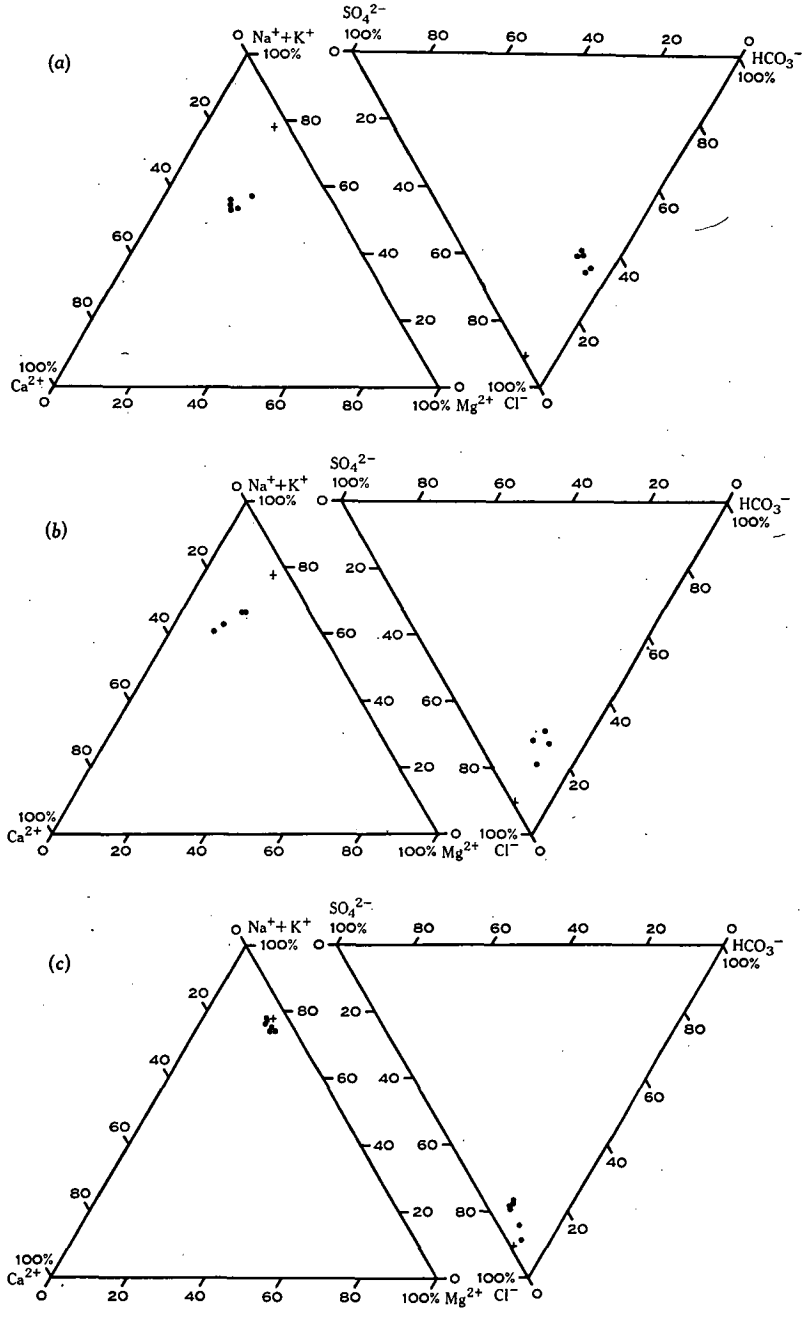

Fig. 3. Ternary diagrams of cationic and anionic proportions of selected Macquarie Island Lakes, showing extent of seasonal variations. (*a*) Square Lake; (*b*) Waterfall Lake; (*c*) Prion Lake.

Square Lake and Waterfall Lake are again aberrant with, additionally, Skua Lake and Skua Tarn. Excluding these lakes, the relationship between Ca^{2+} and O.O.F. for both series of samples is m-equiv. $Ca^{2+}/100$ g = 23·36–0·19 (O.O.F.).

(7) Calculation of enrichment coefficients (after Sugawara 1965) shows that there is no significant enrichment with magnesium, compared with seawater, in any of the lakes.

(8) A plot of total ionic concentration against shortest distance from the west coast shows the same relationships as previous samples (Tyler 1972, Fig. 20). Square Lake and Green Gorge Tarn are, again, furthest displaced from the line. (There is an error in the horizontal axis of Tyler's (1972) Fig. 20—the km values should be multiplied by 2·5).

(9) There is strong positive correlation between total ionic concentration and specific conductivity, and

$$\Sigma^+ + \Sigma^- = 0{\cdot}0183(K_{18}) + 0{\cdot}2822.$$

The slope of 0·0183 obtained statistically from all present and previous samples (including those from Kerguelen) agrees well with the 0·0193 obtained visually with previous samples alone.

Ternary diagrams (Fig. 3) show that seasonal variation in chemical composition is not large. Waterfall Lake is the most variable in this respect, and also in terms of total ionic concentration. Variation is minimal in Square Lake, perhaps because of buffering by sediments in this shallow lake. The greater variability of the deep Waterfall Lake must result from interaction of a varying hydrological regime with a geochemical influence.

We are unable to explain the anomalous position of Square Lake, Waterfall Lake, Skua Lake and Skua Tarn on Fig. 19 of Tyler (1972). The premise underlying this figure is that the most likely geochemical modification of seawater proportions is accession of Ca^{2+} and HCO_3^-, because calcium carbonate is easily dissolved from the soil by carbonic acid. In this case calcium and bicarbonate should accrue in equivalent amounts, and certainly the regression Ca^{2+} on HCO_3^- for all Macquarie Island samples shows strong correlation ($P < 0{\cdot}001$), with $Ca^{2+} = 0{\cdot}014 + 0{\cdot}828\,(HCO_3^-)$. Therefore, a plot of calcium percentage against O.O.F. should be a straight line with negative slope.

The source of calcium bicarbonate enrichment is equally enigmatic. One possibility is local outcrops of weatherable rocks but there are no data to indicate this. The latest map available, based mostly on observations of coastal outcrops (Varne and Rubenach 1972), omits surface deposits. The possibility of groundwater circulation should be considered. One certainty remains—oceanic spray is an important supplier of ions to aquatic and terrestrial ecosystems of Macquarie Island and other Sub-Antarctic Islands (Gorham and Cragg 1960; Tyler 1972; Taylor 1974).

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